Role of Glucose and Related Compounds in Micellar and Nonmicellar Nucleophilic Reactions

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The decomposition of 2,4-dinitrofluorobenzene (DNF) and 2,4-dinitrochlorobenzene (DNC) in aqueous NaOH and cetyltrimethylammonium bromide (CTABr) is speeded by added glucose and the kinetic form and spectral evidence suggest that an intermediate ether is formed and decomposes to 2,4-dinitrophenoxide ion. This intermediate is also formed in the absence of CTABr. The reaction in CTABr is also speeded by methyl α-glucoside and sorbose. The rate constants for the reaction of DNF with OH^- and the anion of the sugar and the decomposition of the ether can be separated by following the reactions at an isosbestic point and at λ_{max} for 2,4-dinitrophenoxide ion. Meisenheimer complexes are detected spectrally in reactions of glucose, sorbose, and sorbitol in the presence of CTABr, and the sorbitol complex is long-lived. Glucose also speeds the reaction of DNF in micelles of *p*-octyloxybenzyltrimethylammonium bromide. Glucose inhibits the reactions of glycyl glycinate with DNF in CTABr and of *p*-nitrophenyl diphenyl phosphate with fluoride and hydroxide ion. These polyols inhibit reaction by a medium effect, but their anions may react nucleophilically.

The effect of chemically inert solutes on micellar catalysis in water has been studied extensively,[3] and generally both electrolytes and nonpolar solutes decrease catalysis.[5,8,9] The effect of added electrolytes can be rationalized in terms of a competition between an inert counterion and a reactive ion for the micelle with some possible effect due to changes in micellar structure.[8,10] Nonionic hydrophilic solutes disrupt micelles, and hydrophobic solutes enter them and reduce the surface charge. Both effects should reduce micellar catalysis. Several monosaccharides apparently increase the catalysis by micellized cetyltrimethylammonium bromide (CTABr) of the reaction of 2,4-dinitrochlorobenzene (DNC) with hydroxide ion.[11] This interesting observation was unexpected and appeared to be an important exception to the well-documented examples of inhibition of micellar catalysis by inert solutes.[5-7] It was suggested that the sugars had a physical effect on the micellar structure but no evidence was given.

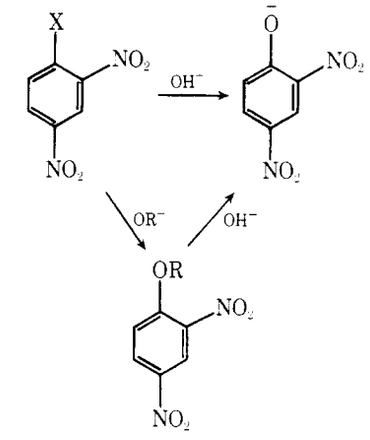
Alkoxide ions are good nucleophiles, even in water,[12] and the 1-hydroxyl groups of sugars have $pK_a \sim 12$,[13,14] so that at high pH an alkoxide ion might react with the halonitrobenzene. Attack of alkoxide ion occurs readily in water at high pH with both DNC and 2,4-dinitrofluorobenzene (DNF) in the presence of β-trifluoroethanol, propargyl alcohol, or choline, and with DNF the formation of the intermediate is much faster than its subsequent decomposition to products, although this is not so with DNC.[15]

The anion of a micellar bound sugar should be a good nucleophile. For example, micelles of alkyl(2-hydroxyethyl)-dimethylammonium bromide and related compounds are effective nucleophiles at high pH in nucleophilic aromatic substitution,[15] addition to carbocations, and dephosphorylation and deacylation.[16] It therefore seems probable that the rate enhancements reported in ref 11 are due to a chemical intervention by the sugar and not to a physical effect on the micelle.

If the beneficial effect of a sugar upon micellar catalysis has a physical origin it should be observed with a variety of nucleophiles, such as fluoride ion or amines, which react at relatively low pH, but if the sugar acts as a nucleophile the effect should be seen only at high pH where the sugar is partly ionized.

We therefore examined the effects of added D-glucose upon the micellar-catalyzed reactions of hydroxide ion and glycylglycine with DNF[17] and hydroxide and fluoride ion with *p*-nitrophenyl diphenyl phosphate.[18] Rates are increased when the sugar can react as a nucleophile, otherwise we observe inhibition.

D-Glucose was used in most experiments, but we used other



X = Cl, F
R = CH_2CF_3, $CH_2C{\equiv}CH$, $CH_2CH_2N^+Me_3$, glucosyl, $CH_2CH_2N^+Me_2C_{16}H_{33}$

polyols including methyl α-glucoside, whose 1-hydroxyl group is blocked. Glucose also speeds the reaction of DNF in aqueous sodium hydroxide and reaction intermediates are detected spectrally in the presence and absence of micelles.

Experimental Section

Materials. The reactants and CTABr were purified following procedures already described.[15] *p*-Octyloxybenzyltrimethylammonium bromide (OOBTABr) was prepared by reducing *p*-octyloxybenzoic acid to the alcohol ($LiAlH_4$), converting the alcohol into the bromide (PBr_3/Et_2O), and quaternizing the bromide with Me_3N in MeCN. The bromide was precipitated (Et_2O) and recrystallized (Me_2CO–Et_2O). This surfactant in water had cmc = 6.9×10^{-3} M, and there was no minimum in a plot of surface tension against concentration. (Found: C, 60.3; H, 9.1; N, 3.7; Br, 22.1. $C_{18}H_{32}NOBr$ requires: C, 60.3; H, 9.0; N, 3.9; Br, 22.3.)

Kinetics. All the reactions were followed spectrophotometrically at 25.0 °C, using solutions made up so that CO_2 was excluded. Solutions were freshly made up because glucose is unstable at high pH, and its decomposition is speeded by micelles of CTABr.[11] The reaction of glyclyglycine with DNF was followed at 355 nm, and that of *p*-nitrophenyl diphenyl phosphate with OH^- or F^- was followed at 403 nm. The formation of 2,4-dinitrophenoxide ion from DNF was followed at 358 nm, but we observed isosbestic points for the reaction of DNF in NaOH with several sugars both in water and in the presence of CTABr (cf. ref 15). Isosbestic points were at the following wavelengths: for DNF with glucose 329–330 mm, methyl α-glucoside 330 nm, and sorbose 327 nm, and for DNC with glucose 330 nm. We obtained good first-order rate constants for the reactions of DNF when reaction was followed at the isosbestic point but generally not when it was followed at 358 nm. However, the final part of these runs followed a first-order rate equation.

There was also a species with λ_{max} at 495 nm which built up during

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Table I. pK_a of Glucose [a]

[glucose], M	pK_a	[glucose], M	pK_a
0.01	12.38	0.15	12.30 (12.28)
0.03	12.31	0.30	(12.24)
0.07	12.30 (12.23)	0.50	(12.20)
0.10	12.32		

[a] At 23 °C with stoichiometric concentration of NaOH of 0.01 M. The values in parentheses were obtained using 0.02 M NaOH.

Table II. Inhibition of Glucose of the Reaction of *p*-Nitrophenyl Diphenyl Phosphate with Hydroxide Ion [a]

[glucose], M	10^3k_Ψ, s^{-1}	[glucose], M	10^3k_Ψ, s^{-1}
	3.80	0.05	2.33
0.01	3.42	0.07	2.27
0.03	2.78	0.10	2.17

[a] At 25.0 °C in 0.01 M NaOH.

Table III. Effect of Glucose on the Reaction of DNF with Hydroxide Ion [a]

[glucose], M	$10^3(k_1^{OH}[OH^-] + k_1^{GO}[GO^-])$ s^{-1} [b]	$10^3k_2[OH^-]$ s^{-1} [c]
	2.58[d]	
0.01	5.32	0.23
0.02	8.50	
0.03	8.03	0.14
0.07	7.87	0.097
0.10	6.89	0.064
0.15	6.47	0.050
0.30	5.14	
0.50	3.90	
0.70	3.94	

[a] At 25.0 °C with 0.02 M NaOH. [b] Followed at the isobestic point at 329 nm. [c] Final part of the reaction followed at 358 nm. [d] 10^3k_Ψ = 2.4 for reaction followed at 358 nm.[18]

reaction. The absorbance in this region was small for reactions of DNF in the presence of glucose and sorbose, but it was large in the presence of sorbitol.

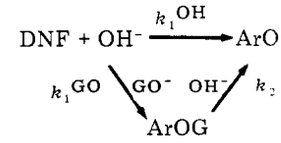
Acid Dissociation of Glucose. We calculated the pK_a of glucose from the change of pH when glucose is added to dilute NaOH using a Thomas high pH glass electrode and a Corning Model 12 pH meter with an expanded scale. Our values are classical and assume no effect of glucose on K_w for water. Within experimental error the pK_a values do not depend on the concentration of added glucose and decrease slightly with increasing initial concentration of hydroxide ion (Table I). Our pK_a values agree reasonably well with literature values of 12.43 at 18 °C and 12.18 at 16.5–19 °C.[13,14]

Results

The general approach was to follow three types of reactions: Type 1 reactions were run at relatively low pH using nucleophiles other than hydroxide or alkoxide ion, for example, fluoride ion or amine. Type 2 reactions involve attack of hydroxide or alkoxide ion, but here only the first step of reaction was followed. In Type 3 reactions attack of alkoxide ion gives an intermediate which generates the final detectable products in a second step, e.g., attack upon a halonitrobenzene gives an aryl ether which then decomposes to a dinitrophenoxide ion.[15]

Reactions in the Absence of Surfactant. As an example of a type 2 reaction we examined the effect of glucose upon the decomposition of *p*-nitrophenyl diphenyl phosphate in aqueous sodium hydroxide (Table II). There is a small rate retardation suggesting that glucose (GOH) has a negative solvent effect which overcomes any contribution due to reaction between substrate and GO^- (the reaction of hydroxide ion is slowed by addition of organic solvents[19]).

Scheme I



A type 3 reaction was that of DNF in hydroxide ion. Addition of small amounts of glucose speeds the reaction of DNF in 0.02 M sodium hydroxide followed at the isosbestic point (Table III). In this table the term $k_1^{OH}[OH^-] + k_1^{GO}[GO^-]$ is the first-order rate constant for the postulated attack by OH^- and GO^- (where GO^- is an anion of glucose). The rate constants go through a maximum with increasing glucose concentration, which is the result of attack by the reactive alkoxide ion, GO^-, and a negative solvent effect by glucose. Reactions at the higher glucose concentration (>0.1 M), followed at the isobestic point, were first order for only 2 half-lives, suggesting that more than one intermediate might be formed, and there was a small shift in the isosbestic point during reaction.

The final part of the reaction followed at 358 nm was first order, and the first-order rate constant for this step is $k_2[OH^-]$ (Table III).

Kinetic Analysis of Reaction of DNF in Aqueous Hydroxide Ion. Although there is evidence for formation of a small amount of Meisenheimer complex in reactions of DNF with glucose in CTABr we detected no such complex in water where the reaction follows Scheme I.

The overall first-order rate constant is determined by following reaction at the isobestic point, whereas reaction followed at 358 nm has a complex kinetic form (cf. ref 15). On the assumption that an intermediate ether is formed the value of $k_2[OH^-]$ for decomposition of the intermediate, ArOG, is estimated by following the final part of the reaction at 358 nm after all the DNF has disappeared.

The first-order rate constant for disappearance of DNF is $k_1^{OH}[OH^-] + k_1^{GO}[GO^-]$, where $[OH^-]$ and $[GO^-]$ are the actual concentrations of the ions in the reaction solution. In principle we can separate these constants using the concentrations of OH^- and GO^- calculated from the pK_a of glucose, but there are several problems. (i) Glucose in relatively high concentration has a medium effect on the reactions, cf. Tables II and III, and probably on its own acid dissociation. (ii) Although the 1-hydroxyl group of glucose is the most acidic there may be contributions from reactions of the other hydroxyl groups, for example, methyl α-glucoside reacts with DNF. But in 0.01 M glucose $[GO^-]$ = 0.0044 M from the data in Table I, and if k_1^{OH} has the same value as in water $k_1^{GO} \sim 0.75\ M^{-1}\ s^{-1}$. Thus the anion of glucose is more nucleophilic than OH^- for which $k_1^{OH} = 0.13\ M^{-1}\ s^{-1}$ (Table III), and our results establish that at high pH glucose is an effective nucleophile, despite the statements to the contrary in ref 11.

The intermediate is much less reactive to hydroxide ion than is DNF, and the decrease of $k_2[OH^-]$ with increasing glucose can be ascribed to a medium effect of glucose and a decreasing concentration of hydroxide ion.

In this treatment we have neglected the role of the α and β epimers of glucose. They and the open chain compound will be in equilibrium in our reaction conditions, but the reactions of their alkoxide ions toward DNF generate different nonequilibriating ethers, which could decompose to dinitrophenoxide ion at different rates. However, the rates of attack of hydroxide upon various 2,4-dinitrophenyl ethers do not depend markedly upon the alkyl group (cf. ref 15 and references cited therein), so that the existence of epimeric inter-

Table IV. Inhibition by Glucose of the Reaction of Glycylglycine [b] with DNF [a,c]

[glucose], M	10^2k_ψ, s^{-1}	[glucose], M	10^2k_ψ, s^{-1}
	2.71	0.07	1.43
0.01	2.22	0.10	1.28
0.03	1.78		

[a] At 25.0 °C, pH 9.5 with 0.015 M borate buffer, 0.025 M glyclyglycine, and 0.025 M CTABr. [b] Registry no. 556-50-3. [c] Registry no. 70-34-8.

Table V. Inhibition by Glucose [d] of the Reactions of *p*-Nitrophenyl Diphenyl Phosphate [e] with Fluoride [f] and Hydroxide Ion [a,g]

	10^2k_ψ, s^{-1}	
[glucose], M	NaF[b]	NaOH[c]
	2.84	7.78
0.01	2.69	5.33
0.02		4.56
0.03	2.08	4.78
0.05	1.70	4.13
0.07	1.64	3.58
0.10	1.52	3.17

[a] At 25.0 °C. [b] 0.01 M NaF at pH 9.0, 0.015 M borate buffer, and 0.002 M CTABr. [c] 0.01 M NaOH in 0.003 M CTABr. [d] Registry no. 50-99-7. [e] Registry no. 10359-36-1. [f] Registry no. 16984-48-8. [g] Registry no. 14280-30-9.

Table VI. Effect of Glucose on the Reaction of Hydroxide Ion with 2,4-Dinitrochlorobenzene [a,d]

	10^3k_ψ, s^{-1}	
[glucose], M	330 nm[b]	358 nm[c]
0.01	3.39	5.26
0.02	5.13	6.25
0.04	6.73	7.50
0.07	7.70	6.07
0.10	6.71	5.40
0.15	5.42	4.33

[a] At 25.0 °C with 0.05 M NaOH in 0.02 M CATBr, $10^3k_\psi = 4.2$ s^{-1} in the absence of glucose. [b] Isosbestic point. [c] λ_{max} for 2,4-dinitrophenoxide ion. [d] Registry no. 97-007.

mediates should not seriously complicate our kinetic analysis based on Scheme I.

Micellar-Catalyzed Reactions

Inhibiting Effects of Glucose. It is convenient to consider first type 1 and 2 reactions, because their rates in aqueous CTABr are reduced by added glucose. This is shown by the results for the type 1 reactions of glycylglycine with DNF in CTABr[17] (Table IV) and of fluoride ion with *p*-nitrophenyl diphenyl phosphate (Table V) and for the type 2 reaction of *p*-nitrophenyl diphenyl phosphate with hydroxide ion (Table V).

In these reactions small amounts of glucose are effectively reducing micellar catalysis. Glucose is very hydrophilic and can exert an appreciable effect on water structure and disrupt the micelles. Attack by glucose upon the phosphoryl group is apparently unimportant.

Catalysis by Glucose of Reactions in CTABr. The reactions of DNF and DNC at high pH fall into type 3, and repetitive scanning of the reaction mixture in the ultraviolet region shows that an intermediate builds up and decays during reaction. We follow disappearance of substrate at the isosbestic point for the intermediate ether and 2,4-dinitrophenoxide ion and appearance of 2,4-dinitrophenoxide ion

Table VII. Effects of Glucose on the Reaction of DNF in Hydroxide and CTABr [a]

[glucose], M	$10^3(k_1^{OH}[OH^-] + k_1^{GO}[GO^-])$, s^{-1} [b]	$10^3k_2[OH^-]$, s^{-1} [c]
	100	
0.01	240	3.92
0.02	285	
0.03	282	1.33
0.05	324	
0.07	308	0.63
0.10	334	
0.15	323	0.35
0.20	275	0.22
0.40	183	0.09

[a] At 25.0 °C with 0.01 M NaOH and 0.025 M CTABr. [b] Followed at 330 nm. [c] Followed at 358 nm.

Table VIII. Decomposition of the Ether Intermediate [a,b]

[glucose], M	$10^3k_2[OH^-]$, s^{-1}
0.01	12.7
0.02	11.6
0.04	9.32

[a] At 25.0 °C; reaction followed at 358 nm in 0.05 M NaOH and 0.02 M CTABr. [b] Registry no. 25775-97-7.

formed directly or via the intermediate at 358 nm.

The reaction followed at the isosbestic point is first order with respect to DNC, but that followed at 358 nm is only approximately so, and first-order plots were linear for less than 2 half-lives. In addition the values of k_ψ obtained at the two wavelengths do not agree (Table VI).

The attack of hydroxide or alkoxide ion upon DNF should be much faster than upon an intermediate 2,4-dinitrophenyl ether, cf. Table III and ref 15. The general approach is similar to that described for reaction in the absence of CTABr. Reactions are followed both at the isosbestic point and at 358 nm, and the results are in Table VII.

For reactions of both DNC and DNF the rate constants for disappearance of substrate ($k_1^{OH}[OH^-] + k_1^{GO}[GO^-]$) go through maxima with added glucose, suggesting that it introduces a new reaction path but also has a negative solvent effect.

The second step of the reaction, decomposition of the intermediate, was followed in 0.05 M NaOH for comparison with the observations on the reaction of DNC. Under these conditions the first step of the reaction of DNF is too fast to be followed by conventional methods, but the first-order rate constant, $k_2[OH^-]$ (Table VIII), is slightly larger than the rate constant for disappearance of DNC (Table VI). Aryl ethers are often more reactive to nucleophiles than the corresponding chlorides.[15]

Separation of Rate Constants of First Step. The initial reaction of DNF gives 2,4-dinitrophenoxide ion directly, plus an ether which slowly goes to phenoxide ion. Therefore the overall reaction followed at 358 nm is not first order with respect to DNF and in principle the steps in Scheme I can be separated using a simulator (Appendix) and fitting the variation of 2,4-dinitrophenoxide ion with time to rate constants for the various steps. (In this approach the value of $k_2[OH^-]$ was that determined directly from the last part of the reaction.)

For reaction in CTABr these individual rate constants are in Table IX, and their sum agrees reasonably well with the values determined directly. The rate of attack of hydroxide ion upon DNF decreases steadily with increasing glucose which decreases the concentration of hydroxide ion.

Table IX. Separation of Rate Constants in Reaction of DNF [a]

[glucose], M	$10^3k_1^{OH}[OH^-]$, s^{-1}	$10^3k_1^{GO}[GO^-]$, s^{-1}	Sum Obsd [b]	Sum Calcd
0.01	211	66.7	240	278
0.03	183	142	282	325
0.07	113	217	308	330
0.15	58.3	239	323	297
0.20	41.7	233	275	275

[a] At 25.0 °C in 0.01 M NaOH and 0.025 M CTABr. [b] Table VII.

Table X. Effect of β-Methyl Glucoside [d] on Decomposition of DNF in CATBr [a,e]

[glucoside], M	$10^3(k_1^{OH}[OH^-] + k_1^{RO}[RO])$, s^{-1} [b]	$10^3k_2[OH^-]$, s^{-1} [c]
	100	
0.01	107 (105)	0.16
0.02	(112)	
0.03	121 (118)	
0.05	119 (131)	
0.07	(139)	0.12
0.10	169	0.16
0.15		0.16

[a] At 25.0 °C with 0.01 M NaOH and 0.025 M CTABr. [b] Followed at 330 nm; the values in parentheses were obtained at 358 nm. [c] Followed at 358 nm. [d] Registry no. 709-50-2. [e] Registry no. 57-09-0.

Table XI. Effect of Sorbose [b] on the Decomposition of DNF [a]

[sorbose], M	10^3k_Ψ, s^{-1}	[sorbose], M	10^3k_Ψ, s^{-1}
0.01	175	0.05	133
0.02	233	0.07	132
0.03	151	0.07	132

[a] At 25.0 °C in 0.025 M CTABr and 0.01 M NaOH, for reaction followed at 327 nm; in the absence of sorbose $10^3k_\Psi = 100\ s^{-1}$. [b] Registry no. 87-79-6.

We were also able to fit the kinetic form of the reaction of DNF in 0.01 M glucose and 0.02 M NaOH in water, followed at 358 nm, using the simulator (cf. ref 15), and estimated the following values of $k_1^{OH}[OH^-] = 3.0 \times 10^{-3}$ and $k_1^{GO}[GO^-] = 1.3 \times 10^{-3}\ s^{-1}$. They are in fair agreement with the first-order rate constant of $5.32 \times 10^{-3}\ s^{-1}$ for disappearance of DNF followed at the isosbestic point of 329 nm.

Effect of α-Methyl Glucoside on Reaction of DNF. Glucose is probably most reactive at the 1-hydroxyl group but there may be contributions from reaction at other positions, because methyl α-glucoside speeds the decomposition of DNF giving an intermediate which decomposes to 2,4-dinitrophenoxide ion (Table X).

In α-methyl glucoside the 6-hydroxyl group should be the most accessible, but reaction of cycloamyloses occurs at the 2-hydroxyl group.[23]

Effects of Other Polyols and Formation of Meisenheimer Complexes. Meisenheimer complexes are formed in some of these reactions, because we observe absorbances at 495 nm which go through maxima in reactions of DNF with glucose or sorbose in CTABr. Cyclic Meisenheimer complexes of 1,2 diols with 2,4-dinitrobenzenes have extinction coefficients at this wavelength of ca. 26 000.[21] If we use this value we estimate that in 0.025 M CTABr and 0.01 M NaOH the reaction of DNF with 0.1 M glucose or sorbose gives a maximum of ca. 5% of Meisenheimer complex. We neglect this relatively small contribution to the overal reaction in our kinetic treatment (Scheme I). We see no absorbance at 495 nm in reactions of methyl α-glucoside with DNF.

Table XII. Effect of Sorbitol [b] on the Decomposition of DNF [a]

[sorbitol], M	10^3k_Ψ, s^{-1} λ 358 nm	λ 495 nm	[sorbitol], M	10^3k_Ψ, s^{-1} λ 358 nm	λ 495 nm
0.01	104	91	0.05		185
0.02	100	91	0.07	183	207
0.03	121	94	0.10	210	233

[a] At 25.0 °C in 0.025 M CTABr and 0.01 M NaOH. [b] Registry no. 50-70-4.

Table XIII. Catalysis of the Reaction of DNF with Hydroxide Ion by OOBTABr [a,b]

10^3[OOBTABr], M	10^3k_Ψ, s^{-1}	10^3[OOBTABr], M	10^3k_Ψ, s^{-1}
	1.2	25	34.0
6	1.56	30	35.0
10	9.26	40	35.3
20	23.5	60	33.3

[a] At 25.0 °C in 0.01 M NaOH. [b] Registry no. 69405-78-3.

Table XIV. Effect of Glucose on the Decomposition of DNF in OOBTABr [a]

[glucose],	$10^3(k_1^{OH}[OH^-] + k_1^{GO}[GO^-])$, s^{-1} [b]	$10^3k_2[OH^-]$, s^{-1} [c]
0.01	88.9	1.77
0.02	107.0	1.04
0.03	112.0	
0.05	126.0	
0.07	128.0	0.46

[a] At 25.0 °C with 0.01 M NaOH and 0.03 M OOBTABr. [b] Followed at 330 nm. [c] Followed at 358 nm.

Sorbose behaves very much like glucose in that the disappearance of DNF followed at the isosbestic point of 327 nm follows first-order kinetics. The rate constants are in Table XI. The reaction followed at λ_{max} for 2,4-dinitrophenoxide ion is not first order, as expected if it involves formation of an intermediate ether plus a small amount of Meisenheimer complex.

With sorbitol there is ca. 50% formation of a Meisenheimer complex absorbing at 495 nm, based on an extinction coefficient of 26 000.[21] This complex is long lived under our reaction conditions (0.1 M sorbitol, 0.01 M NaOH, and 0.025 M CTABr)[22] but it decomposes at low pH. The reaction is first order when followed at either 358 or 495 nm and the rate constants are similar (Table XII) suggesting that the products do not interconvert extensively during the reaction.

The rate enhancements by sorbitol are similar to those found with sorbose, and the only difference is that this open chain polyol forms a cyclic complex much more readily than do the cyclic sugars, even though both glucose and sorbose can have hydroxyls in a cis 1,2 arrangement.

Reaction in Other Cationic Micelles. These rate enhancements by polyols should be general for reactions in solutions of other cationic surfactants, as shown for OOBTABr (Tables XIII and XIV).

In the absence of glucose the micellar catalysis is approximately half that of CTABr, but added glucose gives very similar rate enhancements of the first step of the reaction, followed at the isosbestic point (330 nm), and there is a second

slow decomposition of an intermediate (Scheme I) which can be followed at 358 nm (Table XIV). The rate constants for this second step decrease as expected with increasing glucose concentration.

Chemical and Physical Effects of Sugars and Related Polyols. Glucose and related compounds increase reaction rates in cationic micelles only when they can react as nucleophiles and introduce a new reaction path which involves an alkoxide ion which is more reactive than hydroxide. This situation is observed in reactions of DNC and DNF but not in dephosphorylation or in reactions followed at relatively low pH.

There is always an additional inhibitory effect which is similar to, but larger than, that of hydrophilic monohydric alcohols.[5-7,17b]

Our evidence relates only to glucose and its methyl glucoside, sorbose, and sorbitol but the effects seem to be general; for example, the largest rate enhancements of the decomposition of DNC in CTAB were by fructose which is more acidic than either glucose or arabinose.[13,14] There is no evidence that these rate enhancements have a physical origin as suggested in ref 11.

The rate reductions which we observe in those systems in which the alkoxide ion of the polyol does not act as a nucleophile are similar to those found on addition of simple monohydric alcohols.[17b] The driving force for micellization, i.e., the hydrophobic effect, depends on the water structure, which is disrupted by polar hydroxylic solutes. As noted in ref 11, glucose and related compounds have marked physical effects on micellar catalysis, but these always appear to be inhibitory, and the rate enhancements observed here and reported in ref 11 are occasioned by introduction of a new chemical reaction.

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Appendix

The kinetic simulation followed the approach used earlier,[15] except that a digital rather than an analogue system was used. The design of the simulator is described elsewhere.[24]

References and Notes

(1) On leave from the Institute of Chemistry, University of Perugia, Perugia, Italy with support of the National Research Council of Italy, and a Nato Research Grant.
(2) On leave from the Faculty of Sciences, University of Chile, Santiago, Chile.
(3) For discussion of micellar catalysis see ref 4–7.
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