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Micellar charge effects as mechanistic criteria in spontaneous hydrolyses of acid chlorides[†]

Clifford A. Bunton*

Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106-9510, USA

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ABSTRACT: Reaction rates in aqueous micelles, treated in terms of a pseudophase model, depend on transfer equilibria between water and micelles and rate constants in each pseudophase. Rate constants of spontaneous reactions of fully micellar-bound substrates are independent of transfer and are those in the micellar pseudophase. They depend on its properties as a reaction region and the sensitivity of the reaction to medium effects. For a wide range of spontaneous reactions there are simple relationships between rate constants and properties of the micellar interfacial region, e.g. apparent polarity and head-group charge, which depend on the reaction mechanism. Aqueous micelles inhibit nucleophilic substitutions at alkyl centers, but rate constants, k^+, in cationic micelles are higher than those, k^-, in anionic micelles for S_N2 reactions and lower for S_N1 reactions. Except for nitro derivatives, hydrolyses of substituted benzoyl chlorides are micellar inhibited and $k^+/k^- \approx 18$ for nitro derivative and ca 0.04 for 4-OMe and Me derivatives, indicating different extents of bond making and breaking in the transition state, but there is no evidence of rate-limiting dissociation in hydrolyses of the latter. For hydrolyses of substituted benzenesulfonyl chlorides, values of k^+/k^- decrease from 21 for the 4-NO_2 derivative to 1.1 for the 4-OMe derivative, indicating dominant bond making. These mechanism-related charge effects are ascribed to charge asymmetries at micelle–water interfaces and zwitterionic sulfobetaine micelles behave very similarly to cationic micelles in these hydrolyses. Copyright © 2004 John Wiley & Sons, Ltd.

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KEYWORDS: acyl chlorides; sulfonyl chlorides; nucleophilic substitution; spontaneous hydrolysis; micellar rate effects; reaction mechanism

INTRODUCTION

Bimolecular reactions involving co-ions are micellar-inhibited and those with counterions are accelerated owing to micelles keeping reactants apart, or bringing them together in the small volume of the micellar interfacial reaction region.[1] Analysis of these rate effects in terms of the pseudophase treatment requires estimation of local concentrations at the micelle–water interface. Various models and experimental methods have been developed to treat this problem, and they involve approximations and assumptions.[2–6] A comprehensive review is given in Ref. 7.

The situation is simpler for spontaneous unimolecular reactions such as decarboxylation, or hydrolyses which may be unimolecular, as in the S_N1 reaction at an alkyl center, or involve the solvent as a nucleophile in an S_N2 reaction. In these situations, reaction rates depend only on substrate partitioning between water and micelles and first-order rate constants, k_w and k_m, in each region.[7] With fully micellar-bound substrates, the first-order rate constant in the micellar pseudophase, $k_m = k_{obs}$, and, if this condition is not satisfied, k_m can be calculated by using the pseudophase treatment of Menger and Portnoy:[8]

$$k_{obs} = (k_w + k_m K_s[D_n])/(1 + K_s[D_n]) \qquad (1)$$

where K_s is the association constant with micellized surfactant (detergent), D_n, whose concentration is that of total surfactant, less that of monomer, which is taken to be the critical micelle concentration (cmc). The concentration of monomer is often overestimated by this approximation because solutes typically lower the cmc, but the error becomes negligible at high surfactant concentration. The association constant may be written in terms of the concentration of micelles, and values then differ by the aggregation number, which is typically in the range 60–100, but is increased by added electrolyte. Equation (1) can be linearized in a reciprocal form,[8] or k_m and K_s can be estimated by curve fitting.

**Correspondence to:* C. A. Bunton, Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106-9510, USA.
E-mail: bunton@chem.ucsb.edu

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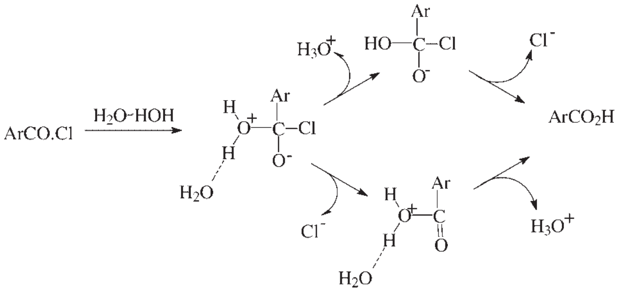
At high surfactant concentration, Eqn (1) simplifies to

$$k_{\mathrm{obs}} = (k_{\mathrm{w}}/\{K_{\mathrm{s}}[\mathrm{D_n}]\}) + k_{\mathrm{m}} \qquad (2)$$

Both Eqn (2) and Eqn (1) in its reciprocal form[8] estimate k_{m} by extrapolation of the data to infinite $[\mathrm{D_n}]$. There is uncertainty in these values, but not in their trend, when reactions are strongly micellar-inhibited, i.e. $k_{\mathrm{w}} \gg k_{\mathrm{m}}$.

Anionic decarboxylations and spontaneous dephosphorylations of dianionic dinitrophenyl phosphates are considerably faster in cationic and zwitterionic sulfobetaine micelles than in water,[9,10] as expected for a medium that is less polar than water. (With anionic micelles these reactions are almost wholly in water.) There is extensive evidence from indicator measurements for this lower polarity of micelles,[11] and it should affect rates of other spontaneous reactions, including hydrolyses at alkyl and acyl centers. These solvolyses can be considered in terms of limiting mechanisms, e.g. for reaction at an alkyl center the slow step can be dissociation, as in the $S_{\mathrm{N}}1$ mechanism, or a concerted nucleophilic attack and loss of the leaving group, as in the $S_{\mathrm{N}}2$ mechanism.[12] Unless the existence of the carbocation can be demonstrated, for example by trapping, it is difficult to exclude borderline mechanisms. A reaction with extensive dissociation and limited bond making in the transition state could have solvent and structural effects typical of an $S_{\mathrm{N}}1$ mechanism, but with nucleophilic participation, or could be regarded as following an $S_{\mathrm{N}}2$ mechanism, but with partial dissociation. Examination of solvent efects does not resolve this mechanistic uncertainty because both $S_{\mathrm{N}}1$ and $S_{\mathrm{N}}2$ solvolyses are generally accelerated by increasing polarity and water content, and with polar protic solvents it is difficult to separate the roles of nucleophilic intervention and solvation of forming ionic centers.[12] In addition, kinetic solvent effects depend on solvent interactions with both the initial and transition states, and kinetic structural and medium effects may therefore not be independent variables, although quantitative treatments involving that assumption fit extensive data.[12b]

This problem of defining the role(s) of nucleophilic solvents becomes more difficult for reactions at acyl centers, where the rate-limiting step could be dissociation giving the acyl cation, although there are few examples of this behavior.[13] In one example, the acid-catalyzed hydrolysis of acetic 2,4,6-trimethylbenzoic anhydride, there is a significant steric effect which favors formation of the trimethylbenzoyl cation.[13a] Bimolecular reactions at acyl centers generally involve attack by an added nucleophile, or a nucleophilic solvent, often assisted by a general base. In one mechanistic limit, addition followed by elimination, attack generates a tetrahedral intermediate which goes to products but, in another limit, nucleophilic attack is concerted with departure of the leaving group, with an $S_{\mathrm{N}}1$–$S_{\mathrm{N}}2$-like mechanism.



Scheme 1

This mechanistic description is illustrated in Scheme 1, following Kevill and co-workers,[14] who included catalysis by a general base, which in the present work is a water molecule. The various reaction steps in Scheme 1 may be concerted, and in some deacylations the initial step may be reversible.[14] In one mechanistic limit the product of addition is shown as an intermediate of finite life, in the other a hydrated acyl cation is formed with loss of Cl^-. These questions regarding extents of bond making and breaking, and the existence of intermediates formed by nucleophilic addition, also apply to spontaneous hydrolyses of sulfonyl and phosphoryl halides. Polar hydroxylic solvent molecules intervene covalently in some of the reaction steps shown in Scheme 1, but interact with partial charges in the transition state, and it is difficult to separate these rate-enhancing interactions.

In discussing possible mechanisms, it is expedient to consider charge locations, although the physical meaning of partial atomic charges is uncertain,[15] especially in water where charge is dispersed into the solvent by hydrogen bonding or by hydration of a cationic center. There is charge asymmetry in the species involved in spontaneous hydrolyses, depending on the mechanism (Scheme 1), and because of the charge distributions at ionic or zwitterionic micellar surfaces there should be relationships between them and reactivities of micellar-bound substrates.

Values of $k_{\mathrm{m}}/k_{\mathrm{w}}$ for spontaneous hydrolyses in micelles and other association colloids vary considerably, depending upon substrate structure and hydrophobicity, and also upon surfactant structure.[7,16–19] Head groups such as carboxylate, which can act as nucleophiles or general bases,[14,17] were not used in this work.

Deacylations are typically accelerated by lyate ions and small amounts of acid (HCl or $\mathrm{MeSO_3H}$) were added to remove adventitious base. All the rate data cited here were obtained at 25 °C. Rate constants in the micellar pseudophase were estimated by using the usual pseudophase formalism[2–5,7,8,16,17] [Eqns (1) and (2)]. Values of k_{obs} in water in the absence of surfactants were measured directly except with electron-donating substituents, which made it necessary to extrapolate data from those in mixed solvents.[16] However, analysis of micellar charge effects is not affected by rate constants in water.[16,17]

RESULTS AND DISCUSSION

Rate constants of spontaneous hydrolyses in aqueous micelles depend on many factors, apart from charge asymmetry across the water–micelle interface. They include polarity, water availability at the interface, head group bulk in cationic micelles and, for S_N1 reactions, the possibility of a common-ion inhibition.[12,13b] It is difficult to isolate the roles of all these factors in a given micelle, but some can be factored out by comparing rate constants in cationic, anionic and sulfobetaine micelles. The anionic micelle was always sodium *n*-dodecyl sulfate, $C_{12}H_{25}OSO_3Na$ (SDS), the cationic surfactants were *n*-hexadecyltrimethylammonium derivatives, $C_{16}H_{33}NMe_3X$ (CTAX), where X is Cl, Br or $MeSO_3$, and the sulfobetaine was $C_{16}H_{33}N^+Me_2(CH_2CH_2SO_3)^-$ (SB3-16), or the C_{14} derivative (SB3-14). The corresponding first-order rate constants for reactions in micelles are designated k^+, k^- and k^{SB}, respectively. Rate constants of spontaneous hydrolyses in the cationic micelles are insensitive to the nature of (nonnucleophilic) counterions, but are sensitive to head group bulk.[7] Discussion of reactivities in cationic and sulfobetaine micelles is limited to those with methylammonium head groups, in the absence of electrolytes which may perturb micellar structure.[4–7]

Values of k^+/k^- and k^{SB}/k^- for reactions of benzoyl and sulfonyl chlorides are given in Tables 1 and 2, and others for hydrolyses of chloroformates and activated esters and at alkyl centers are in the referenced literature.[7,16–19] Reactions at alkyl centers are micellar inhibited, but $k^+/k^- < 1$ for S_N1 and >1 for S_N2 reactions, without exception, although individual rate constants, relative to those in water, vary considerably, depending, in part, upon substrate hydrophobicity which may control location at the micelle–water interface. Cationic and sulfobetaine micelles behave similarly because of similar charge asymmetries in the micelle–water interface, i.e. sulfobetaine micelles behave like cationic micelles with overall charge neutralization. In cationic micelles, head-group charge is largely neutralized by anions in the Stern layer. In general, sulfobetaine micelles have only a modest affinity for anions and the salt order is similar to that for cationic micelles, but ClO_4^- is strongly bound[20,21] (F. Nome, personal communication).

Table 1. Micellar effects on hydrolyses of benzoyl chlorides

		k_m (s^{-1})		
	k_w (s^{-1})	CTACl	SDS	k^+/k^-
3,5-$(NO_2)_2$	0.20	>0.5	0.062	>8
4-NO_2[a]	0.053	0.11	0.0062	18 (24)[a]
4-Cl	0.214	0.012	0.003	4
4-Br[a]	0.190	0.009	0.0025	3.6 (4.3)[a]
4-H	1.41	0.004	0.015	0.27
4-Me	5	0.0015	0.041	0.038
4-OMe	~11	0.01	~0.4	<0.03

[a] At 25.0 °C. Values in parentheses are for k^{SB}/k^- for reaction in SB3-16, where $k_m = 0.013$ and $0.15\,s^{-1}$ for the 4-Br and 4-NO_2 derivatives, respectively.

Table 2. Micellar charge effects on hydrolyses of sulfonyl chlorides at 25 °C

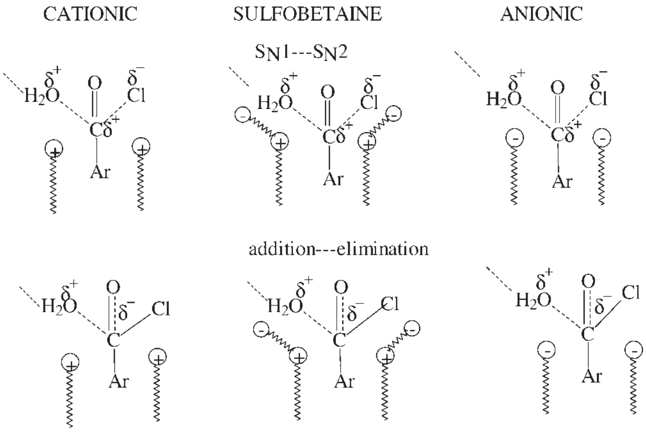
	Substituent				
Parameter	4-NO_2	4-Br	4-H	4-Me	4-OMe
$10^4 k_{CTACl}$ (s^{-1})	21	4.1	1.6	1.0	0.85
$10^4 k_{SDS}$ (s^{-1})	1.0	0.75	0.3	0.35	0.75
$10^4 k_{SB}$ (s^{-1})	22	3.6	1.5	1.0	0.85
k^+/k^-	21	5	5	3	1.1
$10^4 k_w$ (s^{-1})	24.5	19.6	30.7	38.6	61.0

Reactions at acyl centers

The timing of addition and elimination steps in spontaneous hydrolyses of carboxylic anhydrides, chloroformates and acyl, sulfonyl and phosphoryl halides depends upon electronic substituent effects, the nature of the leaving group and, for mixed solvents, polarity and water content.[14,16–18,22,23] As a result, substituent effects, as indicated by Hammett ρ values, are solvent sensitive and some Hammett plots pass through extrema.[22] Hydrolyses of carboxylic anhydrides are general base catalyzed, consistent with an association–elimination mechanism, although this catalysis can be obscured by nucleophilic attack generating a more reactive acyl derivative.[14] Solvolyses of substituted benzoyl chlorides are sensitive to both solvent composition and substituent electronic effects.[16,22] With electron-donating substituents, e.g. alkyl and alkoxy, rates increase significantly with increasing water content of the solvent, but the increase is small with strongly electron-withdrawing substituents, e.g. NO_2, and in some solvents Hammett plots pass through minima.[16,22]

Hydrolyses of most acyl derivatives, including carboxylic anhydrides and diaryl carbonates, are micellar inhibited, except for some nitro derivatives,[16–19] but reactions are faster in cationic and sulfobetaine than in anionic micelles. The pattern is similar for hydrolyses of substituted benzoyl chlorides in that $k^+/k^- > 1$ for nitro derivatives but is <1 for methyl and methoxy derivatives.[16] These variations of k^+/k fit the assumption that strongly electron-withdrawing groups favor an addition–elimination mechanism, with development of negative charge in the acyl moiety (Scheme 1), but with strongly electron-donating sustituents loss of halide ion becomes more important kinetically. The reaction is then concerted with attack on a cationoid acyl group, as in S_N1–S_N2 borderline reactions at alkyl centers when there is no evidence for a carbocationic intermediate.[12]

Comparison of values of k^+/k^- and k^{SB}/k^- in hydrolyses of benzoyl and sulfonyl chlorides is informative because hydrolyses of the latter are micellar inhibited and unlikely to follow dissociative mechanisms, but in CTACl and SB3-16 k^+/k^- and k^{SB}/k^- increase monotonically with increasing electron withdrawal by substituents, and in SDS they pass through a shallow minimum.[17] The substituent order upon k^+/k^- is as for benzoyl chlorides. In general micelles have similar effects upon hydrolysis rates of chloroformates and benzoyl chlorides.[18c,19a,b,d]



Scheme 2

Interactions of the transition state for hydrolysis of a benzoyl chloride with micellar head-groups are illustrated in cartoon form in Scheme 2. The transition state is written as either an anionoid tetrahedral intermediate or, as in a concerted S_N1–S_N2 borderline mechanism, with a cationoid acyl center. Counterions are not shown, but they partially neutralize head-group charges and charge asymmetries are therefore similar in cationic and sulfobetaine micelles. The positive charge in the nucleophilic water molecule is dispersed into other solvent molecules by hydrogen bonding (broken line), and the partial charges, δ^+ and δ^-, on the nucleophilic water, the leaving Cl^-, and the reaction center, are without numerical significance and depend on electronic substituent effects.

Similar descriptions can be applied to other hydrolyses, including those of sulfonyl chlorides and chloroformates in micelles, and with all these substrates the aryl groups should be located in the outer alkyl group regions close to the head-groups.[18b]

Quantification of partial charges in the transition states

Rate constants are considered for reactions that are wholly in the micellar interfacial regions and depend upon the properties of these regions as reaction environments, as distinct from the bulk solvent.[4,5] Attention is directed specifically to charges at the interface. Acid–base equilibria are also sensitive to micellar charge, and dissociations of weak acids, with transfer of unit charge, are increased by cationic and decreased by anionic micelles.[24,25] Comparison of micellar effects on indicator equilibria with those on spontaneous hydrolysis rates provides estimates of fractional charge development at the reaction center. Non-coulombic interactions, such as hydrophobicity, for benzoyl and sulfonyl chlorides should depend largely on the aromatic residue.

Rate constants of spontaneous reactions in water and micelles are given by

$$k_m/k_w = K^{\neq}/K\text{s} \tag{3}$$

following the Eyring treatment, where the equilibrium constants are for transfers of the activated complex and substrate between water and micelles, and can be separated into electrostatic and apolar terms, K_{el} and K_{apolar}, respectively. For reactions in CTACl and SDS, Eqn (4) describes the relationship between k^+/k^- and the equilibrium constants for transfers:

$$\begin{aligned} k^+/k^- &= \{(K^{\neq}_{el}K^{\neq}_{apolar})^+/(K^{\neq}_{el}K^{\neq}_{apolar})^-\}(K_s^-/K_s^+) \\ &\approx (K^{\neq}_+/K^{\neq}_-) \end{aligned} \tag{4}$$

because, to a first approximation,

$$(K^{\neq}_{apolar})^+/(k^{\neq}_{apolar})^- \approx K_s^+/K_s^- \tag{5}$$

for structurally similar substrates. With this simplifying assumption regarding cancellation of the apolar terms, and their separation from the electronic terms, relative rate constants for substrates of similar structures can be related to differences in apparent surface potentials of micelles of CTACl and SDS. The treatment,corresponding to that applied to acid–base equilibria,[24,25] gives

$$\log(k^+/k^-) = \log(K^{\neq}_+/K^{\neq}_-) = \Delta\psi(\delta_Q)/58 \tag{6}$$

where $\Delta\psi$ is the sum of the absolute values of the surface potentials and δ_Q is the apparent fractional charge in the transition state.

Surface potentials are not measured directly, but are inferred from experimental measurement or calculated theoretically.[5,24,25] On an assumed relationship between micellar effects upon acid–base equilibria and surface potentials, Fernandez and Fromherz estimated $\psi = +148$ and -134 mV for CTACl and SDS, respectively,[24] i.e. $\Delta\psi = 282$ mV represents the electrostatic contribution for transfer of one unit of charge. Therefore, for a given reaction, e.g. a spontaneous hydrolysis, and following the formalism of Fernandez and Fromherz[24], Eqn (6) gives

$$\log(k^+/k^-) = (282/58)\delta_Q = 4.9\delta_Q \tag{7}$$

Table 3. Fractional charges at reaction centers in hydrolyses of acid chlorides

	Substituent						
Charge	3,5-$(NO_2)_2$	4-NO_2	4-Cl	4-Br	4-H	4-Me	4-OMe
δ_Q (ArCOCl)	< -0.2	-0.25	-0.12	0.11	0.13	0.29	> 0.31
δ_Q ($ArSO_2Cl$)		-0.27		-0.15	-0.14	-0.093	-0.009

where δ_Q indicates the fractional electronic charge as sensed by the interfacial reaction region. Other assumptions about micellar surface potentials affect values of δ_Q, but not their general trend. For example, the absolute values increase by $\sim$40% if potentials of both CTACl and SDS are taken as 100 mV rather than those in Ref. 24. This procedure compares charge development at the reaction center with the unit change of charge in an acid–base equilibrium.

Values of δ_Q for hydrolyses of the 3,5-$(NO_2)_2$ and 4-OMe derivatives in CTACl and SDS, respectively, are lower limits because they depend on those rate constants which are underestimated because the reactions, in either water or micelles, are too fast for estimation of k_{obs} with fully bound substrate (Table 1and Ref. 16), but they indicate that the absolute fractional charges in the transition states are lower than those corresponding to complete nucleophilic addition to the dinitro derivative or complete ionic dissociation of the methoxy derivative. Variations in these fractional charges follow electronic substituent effects with a change from a cationoid to an anionoid reaction center with increasing electron withdrawal. These estimates of fractional charge indicate that hydrolyses of benzoyl chlorides do not follow a classical S_N1 mechanism in aqueous media. The situation is different for reaction in formic acid, where low nucleophilicity and high acidity, or strong hydrogen bond donation,[22] can change the molecularity of the reaction and promote an ionization mechanism.[13b]

Application of this treatment to hydrolyses of the sulfonyl chlorides indicates that the fractional charge at the reaction center is almost zero for the 4-OMe derivative but is significantly negative for the 4-NO_2 derivative (Table 3). The variations are consistent with hydrolyses following a concerted mechanism with anionoid reaction centers in the transition states, but with contributions of bond breaking increasing on going from the 4-NO_2 to the 4-OMe dervative, and no indication of an ionization mechanism.[17,26]

The two acid chlorides differ in that for benzoyl chlorides the acyl moiety at the reaction center shifts from anionoid to cationoid on going from the nitro derivatives to the Me and OMe derivatives, whereas for the sulfonyl chlorides the corresponding change is from strongly anionoid for the NO_2 derivative to very weakly anionoid for the OMe derivative. The balance between bond making and breaking is more towards the latter in benzoyl as compared with sulfonyl chlorides.

CONCLUSIONS

The role of micellar charge in controlling overall rate constants of ion–molecule reactions is readily understandable in terms of transfers of ionic and non-ionic reactants between water and micelles, but for some spontaneous reactions charge has a significant effect on reactivity in the micellar pseudophase. Charge asymmetries are similar in the interfacial regions of cationic and sulfobetaine micelles, which assists spontaneous decarboxylations and dephosphorylations where electronic charge moves the ionic residue into the organic moieties during formation of the transition states.

In spontaneous bimolecular hydrolyses, charge moves from nucleophilic water into the reaction center and the leaving anion, depending on extents of bond making and breaking in the transition state. In one limiting mechanism for reaction at acyl centers an addition intermediate is formed and then dissociates to products, and in another limit ionization gives a cationic intermediate in the rate-limiting step, but these limits appear not to be reached for reactions in water. The association–dissociation balance depends upon substrate structure and the reaction environment, but relative rate constants in anionic and cationic or sulfobetaine micelles are indicators of this balance for hydrolyses of structurally similar substrates differing only in substituent electronic effects. For hydrolyses of the acid chlorides discussed here, there is no indication that the rate-limiting step is formation of an addition intermediate from the nitro derivatives or formation of an acyl cation from 4-methoxybenzoyl chloride. The reactions appear to be concerted with the balance between bond formation and dissociation depending on the reaction center and electronic effects of substituents. This mechanistic test requires that reaction sites are the interfacial regions of normal micelles, and is therefore restricted to reactions in water as the bulk solvent, although the general mechanistic conclusions should be applicable to solvolyses in water-rich mixtures where ion pairing is unimportant. It is not applicable to reactions in weakly nucleophilic or low-polarity solvents where ion pairing and other interactions can be dominant.

Supplementary Material

Reactions were followed spectrophotometrically in water as described in references 16 and 17.

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