

was filtered off and washed with pentane, giving 14.4 mg (0.091 mmol) of orange 1,2-naphthoquinone, sintered 125 °C, mp ca. 133–139 °C dec. Melting points between 121 and 146 °C are cited in the literature.¹⁹ The IR spectrum (Nujol mull) matched a published one except for a small systematic shift in the wavelengths.²²

For quantitation, 90 μ L of 0.425 M 2-naphthol in ether was injected into 1.05 mL of 0.15 M 1 in hexane. After 5 min, the mixture was diluted to 4.0 mL. This solution showed λ_{max} 536 nm (abs = 0.28), and the absorbance at 800 nm was 0.034. A 0.0162 M solution of the quinone in ether showed λ_{max} 536 nm (abs = 0.578). From these data and $\epsilon = 4.7$ at 800 nm for 1 (in cyclohexane), we calculated that 4.1 mol of 1 was consumed per mole of the quinone produced, assuming that the ϵ values were unchanged by the slight differences in solvent.

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9-Phenanthrol. Aldrich technical grade product was partially purified by sublimation at <1 torr. From 52.8 mg (0.272 mmol) of phenanthrol and 5 equiv of 1, a yellow orange precipitate was obtained. After standing at 25 °C for 17 h, it was filtered off and washed with pentane: 28.6 mg, mp 205–207 °C (lit.¹⁹ mp 208–210 °C). The IR spectrum matched a published spectrum of 9,10-phenanthrenequinone.²²

The filtrates at -16 °C deposited 33.4 mg of pure 1-H (¹H NMR, mp), and a further crop was isolated on cooling to -60 °C (23.0 mg after crystallization from aqueous MeOH).

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Structural Effects Affecting Hydration of 1,2-Diones Studied by Linear-Sweep Voltammetry¹

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Linear-sweep voltammetry was used for determination of values $K_d^{\text{CO}} = [\text{RCOCOR}]/[\text{RCOC(OH)}_2\text{R}]$ and $K_d^{\text{COH}} = [\text{RCOCOH}^+\text{R}]/[\text{RCOC(OH)(OH}_2^+\text{)R}]$ for some aliphatic and alicyclic 1,2-diketones. Values obtained were compared with data obtained from UV and NMR spectra. Dc polarographic data were used to choose the most reliable value. In all cases, the protonated form predominating in solutions of sulfuric acid is less strongly hydrated than the unprotonated form. The effect of ring size on the hydration in polycyclic species is discussed. Steric hindrance of the hydration due to the 7- and possibly the 1-methyl group in 2,3-camphorquinone has been confirmed.

Ketones undergo reversible hydration, resulting in formation of geminal diols, much less readily than aldehydes.² Presence of adjacent electronegative groups can, nevertheless, result in an increase in the hydration of the keto group. Effects of alkyl groups, halogenated alkyl groups, and carboxylic groups were successfully treated by a four-parameter linear-free-energy relationship.³ This approach, nevertheless, fails to enable interpretation of the lack of hydration of most benzaldehydes, "neutral" heterocyclic aldehydes, alkyl aryl ketones, diaryl ketones, α,β -unsaturated aldehydes and ketones, or 1,3-diketones. Interpretation of the absence of hydration as due to resonance effects encounters problems of interpretation of strong hydration of all pyridine carboxaldehydes and other formyl derivatives of "basic" heterocycles. Effect of structure on hydration of 1,2-diketones, where the shift in favor of the hydrated form is due to the electron-withdrawing properties of adjacent carbonyl groups, has been discussed only qualitatively⁴ based on the possibility of isolation of the particular hydrate. Sandris and Ourisson⁴

did not have available values of equilibrium constants of the hydration-dehydration reaction but were able to propose that the stability of the hydrate depends on three factors: polar effects of substituents, ring strain, and steric effects of nonbound groups. Presence of halogens increases the stability of the hydrate. Ring strain (Bayer) causes five-membered cyclic 1,2-diketones to be more strongly hydrated than six-membered. Presence of methyl groups in 2,3-camphorquinone prevents formation of a crystallizable hydrate, which is possible for α -santenonequinone, bearing one less methyl group in position 7.

For the course of investigation of electroreduction of 1,2-diketones,⁵ a knowledge of the equilibrium constant of the dehydration reaction ($K_d = [\text{nonhydrated form}]/[\text{hydrated form}]$) proved essential. In the search for a suitable method for determination of these constants, serious limitations were encountered: The use of UV spectra for the study of hydration of carbonyl compounds involves⁶ an estimate of the molar absorptivity of the free carbonyl form. This always introduces a degree of uncertainty, but for 1,2-diketones, the situation is complicated by the unusual dependence of UV spectra on solvent composition.^{5b} Thus, for 3,3,6,6-tetramethyl-1,2-cyclohexanedione, the

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absorbance measured at the maximum at about 380 nm changes little when acetone, dioxane, carbon tetrachloride, or *n*-heptane is employed as a solvent and was thus used⁷ in calculation of the constant K_d . But when absorbances at the maximum in the 280-nm range are compared in Figure 2, ref 7, a variation with solvent of about 20% is observed.

¹⁷O NMR was used³ for calculation of the value of K_d for biacetyl, but the value obtained (0.50) differs considerably from values obtained by any other method ($K_d \approx 0.3$). Moreover, the application of NMR methods for the study of other compounds is often limited by their insufficient solubility.

The use of dc polarographic limiting currents was proposed^{7,8} for determination of K_d under the assumption that even under conditions of polarographic electrolysis, the removal of the diketone form does not perturb the equilibrium between the nonhydrated and monohydrated forms. Under such conditions, the limiting current would be directly proportional to the concentration of the free, nonhydrated diketone form in the bulk of the solution. As it has been proved^{5b} that the limiting current of 2,3-camphorquinone is partly governed by the rate of dehydration rather than only by diffusion, as assumed earlier,⁸ and as the dependence of the limiting current of 3,3,6,6-tetramethyl-1,2-cyclohexanedione on temperature at pH < 8 (Figure 6, ref 7) indicates that the same applied to this diketone, the assumption that the limiting currents are proportional to the equilibrium concentration of the free dicarbonyl form leads to erroneous values of K_d .

Thus, a linear-sweep voltammetric method,⁹ in which the voltage sweep occurs so rapidly that the equilibrium between the hydrated and nonhydrated forms is practically not perturbed, was chosen for the determination of values of K_d . The current in this case is governed by the rate of diffusion, and the measured peak current is a linear function of the concentration of the free, nonhydrated diketone form present in equilibrium in the solution.

Experimental Section

Compounds and Solutions. Camphorquinone (Aldrich Chemical Co.), 1-phenyl-1,2-propanedione (Aldrich), 1,2-cyclohexanedione (Aldrich), and thallium(I) sulfate (Alfa Inorganic) were all more than 95% pure and used as received. Biacetyl (Eastman Kodak Co.), acetoin (Aldrich), and 2,3-pentanedione (Eastman Kodak) were used after distillation at reduced pressure. The distillate was stored at 5 °C and was stable for up to six months. Both 4,5-homoadamantanedione and 2,3-norbornanedione were synthesized by Dr. R. Partch. 4,5-Homoadamantanedione was used as received, and 2,3-norbornanedione was purified by injection of a sample dissolved in chloroform into a gas chromatograph and collection in glass capillaries. The Diels-Alder adduct of 2,3-naphthoquinone and cyclopentadiene was synthesized by V. Horák (Georgetown University, Washington, DC) and used as received.

Stock solutions were prepared usually as 0.01 M solutions in water (biacetyl, 2,3-pentanedione), 50% ethanol (Diels-Alder adduct, 1-phenyl-1,2-propanedione), 50% acetonitrile (2,3-norbornanedione), 10% Me₂SO (2,3-camphorquinone), or Me₂SO (4,5-homoadamantanedione). Stability of the stock solutions when left in dark at 5 °C varied from 1 day (biacetyl) to 2 weeks (2,3-camphorquinone).

Solutions of sulfuric acid of $H_0 -4.0$ were prepared from a reagent grade acid (Baker Chemical Co.). Acetate buffer, pH 5.6, was prepared from reagent grade acetic acid (Mallinckrodt Chemical Co.) and reagent grade sodium acetate (Baker) so that it contained 0.04 M sodium acetate and 0.04 M acetic acid. Ionic strength was adjusted to $\mu = 0.2$ by addition of sodium chloride.

Apparatus. A voltage ramp generator allowing scan rates from 2 to 2000 V min⁻¹ was used, and the current-voltage curves were recorded on a Tektronix Type 564B storage oscilloscope, equipped with Type 2A63 and Type 3A9 differential amplifiers. A two-electrode Kalousek cell was used in conjunction with a slowly dropping mercury electrode with $m = 0.35$ mg s⁻¹ and natural drop-time $t_1 = 20.1$ s (in 1.0 M KCl at 0.0 V) at $h = 30$ cm as the indicator electrode and SCE, separated by liquid junction, as reference electrode for experiments in acetate buffer, or mercury-mercurous sulfate reference electrode, prepared with concentrated sulfuric acid, for experiments in sulfuric acid solutions. The voltammetric scans were initiated 18 s after the previous drop was dislodged.

Procedures. A 10.0-mL volume of the supporting electrolyte was pipetted into the electrochemical cell and oxygen removed with a stream of nitrogen for 3 min. A sample of stock solution (varying from 50 to 200 μ L, depending on its concentration) was then added to the supporting electrolyte. This solution was then purged with nitrogen for 45 additional seconds and the current-voltage curve recorded.

The final concentrations of the diketone in aqueous solutions with given cosolvent were as follows: 2×10^{-4} M 2,3-camphorquinone with 0.2% Me₂SO, 1×10^{-3} M biacetyl in water, 2×10^{-4} M 2,3-pentanedione in water, 1.03×10^{-4} M 2,3-norbornanedione with 1% Me₂SO, 1.45×10^{-3} M Diels-Alder adduct with 30% (v/v) ethanol, 2×10^{-4} M 1-phenyl-1,2-propanedione with 1% ethanol and 0.2% gelatin for suppressing polarographic maxima, 5×10^{-4} M 4,5-homoadamantanedione with 2% acetonitrile. Solubility and stability of stock solutions lead to choice of various cosolvents.

Results and Discussion

Study of the dc polarography of 1,2-diketones revealed that whereas in the middle pH range the electrolytic current is governed by the rate of the solvent-catalyzed dehydration, in strongly acidic solutions the dehydration occurs via the protonated form of the geminal diol. In the latter case, either the rate of protonation or the rate of the elimination of water from the rapidly formed protonated form can be rate-determining.¹⁰ Such understanding of the observed changes of currents with the acidity of the solution and of the processes involved made it possible to restrict the investigation by linear sweep voltammetry (LSV) to two solutions: In acetate buffer, pH 5.6, the solvent-controlled dehydration predominates for all the 1,2-diketones studied and neither acid- nor base-catalyzed reaction complicates the data treatment. In solutions of 8.2 M H₂SO₄ ($H_0 -4.0$), the rate of the dehydration via the protonated form is sufficiently fast to become the predominant pathway. For 4,5-homoadamantanedione, 4.5 M H₂SO₄ ($H_0 -2.1$) and acetate buffer, pH 3.8, were used.

In both these solutions, all of the diketones studied showed a linear dependence of the measured peak current (i_p) on the square root of the sweep rate (v) (Figure 1), at least over a certain range of sweep rates (Table I). In the absence of reliable values for the diffusion coefficients of the nonhydrated form, it is possible to obtain the values of K_d with use of such data in two ways: Either a measured current of the free carbonyl form, in equilibrium with the monohydrated form, is compared at a given sweep rate (within the range where i_p is a linear function of $v^{1/2}$) with a hypothetical current, which would be obtained for an equimolar solution of a compound present in the studied solution completely in the free, nonhydrated carbonyl

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Table I. Dependence of the Peak Current (i_p) Obtained for 1,2-Diketones by Linear Sweep Voltammetry on the Sweep Rate at 25 °C^a

diketone	sulfuric acid, $H_0 -4.0$					acetate buffer, pH 5.6				
	$di_p/dv^{1/2}$, $\mu A V^{-1/2} min^{-1/2}$	range, V min^{-1}	intercept, μA	αn_a^b	$D^c \times 10^6$, $cm^2 s^{-1}$	$di_p/dv^{1/2}$, $\mu A V^{-1/2} min^{-1/2}$	range, V min^{-1}	intercept, μA	αn_a	
biacetyl	4.5	4-200	2.6	0.84	6.6	1.2	4-100	0.92	0.95	
i,3-pentanedione	1.0	4-200	0	0.84	7.8	0.29	4-100	0	0.92	
2,3-camphorquinone	1.1	4-75	0.12	0.78	8.1 ^d	1.0	4-50	0.1	0.78	
4,5-homoadamantanedione	0.7 ^e	2-20	0.36 ^e	0.83	8.9 ^e	0.4 ^f	2-20	0 ^f	1.3	
2,3-norbornanedione	0.23	9 ^g -100	g	0.80						
Diels-Alder adduct						0.3	16 ^h -200	h	0.87	
1-phenyl-1,2-propanedione	1.4 ⁱ	4-75	0.25	1.28	8.4	0.55	4-200	0.19	1.23	

^a For E_p values and their dependence on pH, see ref 5b. ^b Obtained by logarithmic analysis of dc polarographic curves. ^c Calculated from dc polarographic currents in strongly acidic media by using the uncorrected form of the Ilkovič equation. ^d Calculated from the highest current at pH 11. ^e $H_0 -2.0$. ^f pH 3.8. ^g At $v < 9 V min^{-1}$, current becomes independent of v . ^h At $v < 16 V min^{-1}$, current becomes independent of v . ⁱ $H_0 -5.0$.

Table II. Values of Equilibrium Constants for Hydration-Dehydration Reactions of 1,2-Diketones at 25 °C

$$K_d^{CO} = [RCOCOR']/[RCOC(OH)_2R']$$

$$K_d^{COH} = [RCOCOH^+R']/[RCOC(OH)(OH_2^+)R']$$

diketone	$K_d^{CO a}$	$K_d^{COH b}$	$K_d^{CO c}$	$K_d^{CO d}$	$K_d^{CO e}$
biacetyl	0.30	5.3	0.27	0.32 0.37 ^g 0.30 ^f	<0.32 0.41 ^f 0.47 ^h 0.50 ^j
2,3-pentanedione	0.39	6.3	0.31		<0.52
camphorquinone	17	25	3.8	19 11 ^k	<8.2 <9.5 ⁱ
2,3-norbornanedione		0.92			<0.06
Diels-Alder adduct			0.32		<0.08
4,5-homoadamantanedione		0.29	0.12		<0.64
1-phenyl-1,2-propanedione	0.85	16	0.61		

^a Method A, using naphthoquinones as a model for a diffusion-controlled process. ^b Method B, using limiting currents in strongly acidic media to calculate diffusion coefficients. ^c Method C, from UV spectra in aqueous, unbuffered solutions, ref 5b. ^d Method D, from $i_k/(i_d - i_k)$, ref 5b. ^e Method E, from NMR spectra. ^f K_d^{CO} value at 35 °C, ref 5b. ^g Reference 6. ^h Reference 11. ⁱ Reference 12. ^j Reference 3. ^k Using molar absorptivity in buffered solutions, ref 5b. ^l Follows from data in ref 9, at 20 °C.

form, at the same sweep rate; or, alternatively, the slope of the $i-v^{1/2}$ plot, obtained for the reduction of the free keto form of the studied compound in equilibrium with the geminal diol, is compared with the hypothetical slope of an analogous dependence, obtained under identical conditions for an equimolar solution of a compound present in the solution completely in the carbonyl form.

In both these cases, the data for the hypothetical non-hydrated form are essential and can be a source of errors. In the past, the comparison of currents has been carried out with use of solutions of thallium(I) ions.⁹ The tacit assumption in such treatments has been that the diffusion coefficients of Tl^+ ions and of the organic compound studied are equal. In this study, it was considered that the slope of the $i-v^{1/2}$ plots is less affected by random errors than a value of current measured at one sweep rate. Furthermore, 1,4-naphthoquinone, 2-hydroxy-1,4-naphthoquinone, and 5-hydroxynaphthoquinone were used as model compounds at pH 5.6, as it seemed more probable that the diffusion coefficients of these reversible redox systems are similar to those of the studied compounds than that of Tl^+ ions. The values of the slopes $(di_p/dv^{1/2})_q$ for all three quinones were found to be practically identical and equal to $0.69 \mu A V^{-1/2} min^{-1/2}$ at $c = 1 \times 10^{-4} M$, which enabled calculation of the theoretical slope $(di_p/dv^{1/2})_{theor}$ for the nonhydrated forms of the studied 1,2-diketones (which are quasi-reversible systems):

$$\left(\frac{di_p}{dv^{1/2}}\right)_{theor} = \frac{3.03 \times 10^5 n (\alpha n_a)^{1/2} (di_p/dv^{1/2})_q C_d}{2.74 \times 10^5 n^{3/2} C_q} \quad (1)$$

where the total number of electrons transferred in both cases is $n = 2$, the value of αn_a was obtained by logarithmic

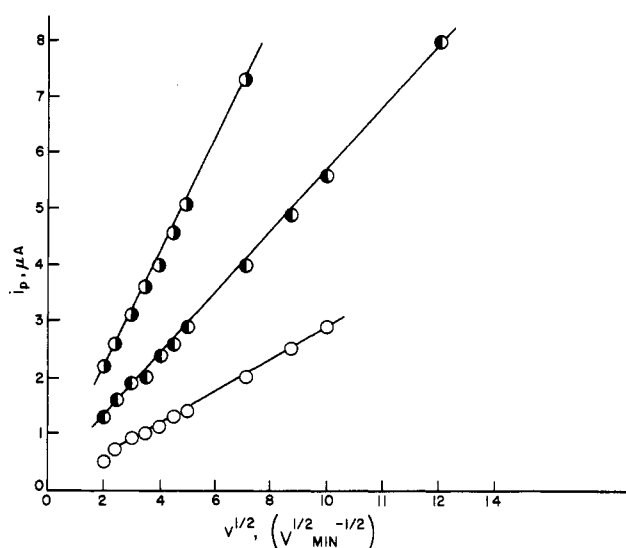


Figure 1. Linear sweep voltammetry of 1,2-diketones in acetate buffer, pH 5.6. Dependence of peak current (i_p) on the square root of the rate of scanning (v) for 2,3-pentanedione, O; 2,3-camphorquinone, ●; and 1-phenyl-1,2-propanedione, ○.

analysis from dc polarographic curves in given solution (Table I), C_d is the concentration of the diketone, and C_q is the concentration of the quinone. K_d^{CO} can then be expressed as

$$K_d^{CO} = \frac{(di_p/dv^{1/2})_d}{(di_p/dv^{1/2})_{theor} - (di_p/dv^{1/2})_d} \quad (2)$$

where $(di_p/dv^{1/2})_d$ is the slope of the i_p vs. $v^{1/2}$ plot for the

studied 1,2-diketone in the given solution. The resulting values are reported in Table II (method A).

Alternatively, the hypothetical current for the free, nonhydrated species $(i_p)_{\text{theor}}$ has been obtained by using eq 3, where the symbols have their above-defined or usual

$$(i_p)_{\text{theor}} = 3.03 \times 10^5 n(\alpha n_a)^{1/2} D^{1/2} C A v^{1/2} (1000 \times 60^{-1/2}) \quad (3)$$

meaning and A is the area of the drop electrode in cm^2 . The value of the diffusion coefficient D was obtained from dc polarographic limiting currents for each particular 1,2-diketone in strongly acidic media, where they are practically controlled by diffusion.⁵ For 2,3-camphorquinone, the limiting current at pH 11 was used instead. From the currents, corrected for the change in viscosity, values of diffusion coefficients D were calculated by using the simple form of the Ilkovič equation (Table I).

By means of the equation

$$K_d = i_p / [(i_p)_{\text{theor}} - i_p] \quad (4)$$

the values of the equilibrium constant of the hydration-dehydration reaction of the unprotonated form (K_d^{CO}) were obtained by using current i_p measured at pH 5.6 and those for the protonated form (K_d^{COH}) by using current i_p measured at H_0 -4.0 (Table II, method B).

For comparison, values of constants K_d^{CO} obtained from UV spectra (method C) and NMR spectra (method E) are given in Table II. Polarographic data (method D) are based on the ratio $i_k / (i_d - i_k)$, where i_k is the limiting current in the pH range where the solvent-controlled dehydration predominates and i_d is the diffusion current obtained in strongly acidic or mildly alkaline medium. As the equilibrium concentration of the free diketo form is lower than that which corresponds to the kinetic current i_k , dc polarographic currents can offer information only about the upper limit of the value of K_d . Nevertheless, dc polarographic data are rather accurate and their use does not involve any assumption or approximation.

Using data obtained by dc polarography makes it possible to make a choice of the best value of the equilibrium constant at least in two cases. For **biacetyl**, the best value of K_d^{CO} seems to be in the range between 0.27 and 0.30. The value of 0.41, obtained by one of us using NMR spectra^{5b} is smaller than other data obtained by this technique (Table II). Nevertheless, all the values obtained by NMR are significantly higher than those obtained by other techniques, which seem to be internally consistent. This may be due to the fact that the NMR measurements (whether proton or ^{17}O) were carried out at concentrations of biacetyl about three orders of magnitude higher than those using electrochemical or spectral data. Under such conditions, biacetyl may not exist in aqueous solutions solely in the monomeric form, or, alternatively, biacetyl can act as a cosolvent and participate in solvent-solute interactions. The role played by such factors makes it questionable to consider in general the data on hydration-dehydration equilibrium constants obtained by NMR^{3,6} superior to data obtained by other techniques. For **2,3-camphorquinone**, larger variations in the values of

K_d^{CO} obtained by various methods (Table II) are observed than for other diketones. This reflects the fact that 2,3-camphorquinone is much less strongly hydrated than the other studied dicarbonyl compounds. Calculation of K_d^{CO} in such cases involves small differences between two large similar values, which results in significant errors. The best value must be smaller (for reasons given above) than the value of $K_d^{\text{CO}} = 9.5$ reported earlier,⁸ and thus $K_d^{\text{CO}} = 3.8 \pm 2$ seems the best estimate.

The position of the hydration-dehydration equilibrium depends on whether the 1,2-diketo grouping is present in a straight chain (60–80% hydrated, Table II) or in a cycle. In cyclic compounds, the ring size and presence of bulky groups in the vicinity of the dicarbonyl function play important roles. The case of cyclohexanedione, where the measurement of the hydration-dehydration equilibrium is complicated by the significant contribution of the enol form, will be put aside. Polarographic evidence⁵ indicates that the diketo form is strongly hydrated. This is consistent with the value of $K_d = 5.5 \times 10^{-3}$ reported earlier,¹³ but this value was obtained in 99% dioxane and it is questionable in how far it can be compared with values (Table II) obtained in predominantly aqueous solutions.

In the other cyclic compounds studied, the diketo form predominates in the solution, as the α -carbons to both carbonyl groups are bridgehead atoms and formation of the enol form would violate Bredt's rule. For such compounds, cyclic 1,2-diketones bearing the keto groups in a five- or six-membered ring are more strongly hydrated (2,3-norbornanedione, 94%, and the Diels-Alder adduct of 2,3-naphthoquinone and cyclopentadiene, 93%) than those bearing the dicarbonyl grouping in a seven-membered ring, as for 4,5-homoadamantanedione (61% hydrate), the behavior of which resembled, more closely, that of the open-chain compounds. On the other hand, in 2,3-camphorquinone (bearing the two keto groups in a five- or six-membered ring), the 7-methyl group that is syn to the dione moiety¹⁴ and possibly also that on carbon 1 exert such a steric hindrance to hydration that the compound is less than about 20% hydrated. The difference of one order of magnitude in the value of K_d^{CO} expresses quantitatively the steric effect qualitatively suggested by Sandris and Ourisson.⁴

As in other cases of carbonyl compounds forming covalent hydrates, the hydration of the positively charged form present in strongly acidic media is much weaker than that of the uncharged form, the value of K_d increasing by a factor of 18 on the average (with extremes of factors of 26 and 7). Even when in the case of 1,2-diketones the role of a polar effect of the protonation on the adjacent carbon cannot be excluded, it may be concluded that protonation of a hydroxy group in the geminal diol form results in a much weaker C–O bond. Alternatively,¹⁴ the decrease in the hydration of the protonated form may be attributed to its resonance stabilization, which is lost upon hydration.

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