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Comparison between the Kinetics of the Alkaline Fading of Carbocation Dyes in Water/Sodium Bis(2-ethylhexyl) Sulfosuccinate/Isooctane Microemulsions and in Homogeneous Media

J. Ramón Leis,* Juan C. Mejuto, and M. Elena Peña

Departamento de Química Física, Facultad de Química, Universidad de Santiago,
15706 Santiago de Compostela, Spain

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The kinetics of the alkaline fading of crystal violet (CV) and malachite green (MG) have been studied in water/sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/isooctane microemulsions and the results compared with those found for the same reactions in homogeneous media. The alkaline fading of crystal violet takes place readily in microemulsions, as observed by the decrease in the 590-nm absorbance due to the consumption of the dye. However, unexpectedly, after some time, the absorbance starts to increase and the original spectrum of crystal violet is recovered. Under most experimental conditions, the original amount of crystal violet is restored after 24–36 h. This peculiar behavior is explained by taking into account the hydrolysis of AOT—a process which consumes OH^- —as well as the reversibility of the reaction between CV and OH^- . This pattern of behavior is not observed in the case of MG, for which the reaction proceeds to the total disappearance of the dye, no further recovery of MG being observed. Measured rate constants for the alkaline fading of both dyes under various experimental conditions suggest that the reaction takes place in the microemulsion water pools, intrinsic reactivity being significantly lower than in pure water. Analysis of the ^1H NMR signals of water protons in microemulsions with and without CV provides evidence for the location of CV within the water pools. Finally, a surprising change in the visible spectrum of CV in water has been observed in the presence of perchlorate ions, and these ions also drastically inhibit the hydrolysis of the dye. This observation has been interpreted as evidence of a specific interaction between CV and ClO_4^- , probably leading to the formation of ion pairs. Spectral changes observed upon incorporation of CV to microemulsions are compared and discussed.

Introduction

The alkaline fading of stable triarylmethyl carbocations is a reaction with a long chemical tradition. The rate for the process—in spite of being a cation-anion combination—is slow enough for a conventional kinetic study, and in fact, the reaction has become a popular one for undergraduate laboratories.¹ Reaction also takes place with nucleophiles other than OH^- , a fact that has been used for the construction of the familiar Ritchie N_+ nucleophilicity scale.² In spite of the many studies made of the mechanism of these reactions, some mechanistic essential details are still confused and the reaction has become one of the main challenges to the reactivity-selectivity principle.^{3–5}

The reaction has also become a useful one for studying chemical reactivity in organized media. One⁶ of the first studies on micellar catalysis and inhibition referred to the alkaline fading of crystal violet (CV), and these reactions have been used later very often for studies in normal micelles,^{7–10} micelles in the presence of additives,^{11–13}

reverse micelles or water-in-oil microemulsions,^{14–18} and clusters.¹⁹ The reaction is typically a “well-behaved” one and has become an interesting source of information on the role of the different factors that affect overall reactivity in normal micelles (i.e., compartmentalization of the reagents, characteristics of the micellar reaction medium). However, the interpretation of results in water-in-oil microemulsions is less straightforward, and in most cases quantitative interpretation of kinetic data was not achieved.

In this paper we report on the surprising results found when studying the alkaline fading of CV in water/sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/isooctane microemulsions, a system which is similar to that used by other researchers when studying the same reaction.¹⁷ For comparative purposes the alkaline fading of the related carbocation malachite green (MG) was also studied, as well as the corresponding reactions in aqueous media.

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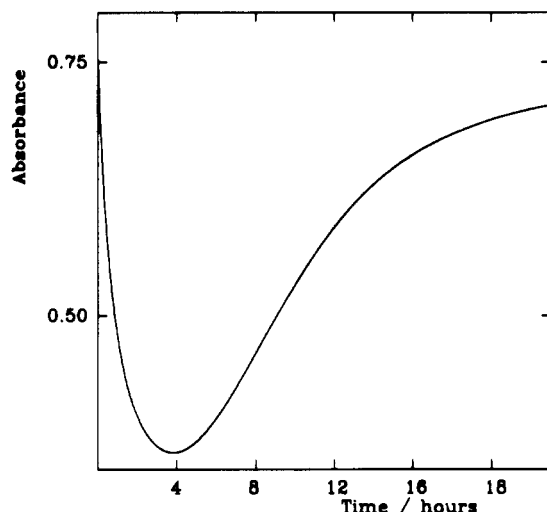


Figure 1. Absorbance (590 nm)-time plot for the alkaline fading of CV in water/AOT/isooctane microemulsions. [AOT] = 0.33 M, $w = 24$, [NaOH] = 5×10^{-3} M, and [CV] = 8.3×10^{-6} M.

Experimental Section

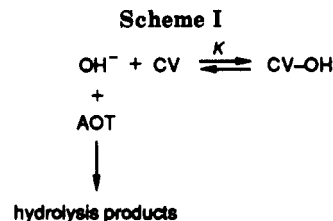
AOT (Sigma) was dried for 2 days in a vacuum desiccator. For some experiments AOT was dissolved in methanol with active charcoal, filtered, and dried in vacuo several times, as described in the literature.²⁰ No difference was observed between the results obtained with this purified AOT and those obtained with the commercial samples. MG was supplied by Aldrich. All other reagents were Merck products of the maximum commercially available purity and were used without further purification. Solutions of NaOH were titrated with potassium hydrogen phthalate.

Kinetic measurements and spectral studies were carried out in a UV-vis Milton Roy Spectronic 3000 diode array spectrophotometer with a thermostated multiple cell holder. All experiments were carried out at 25 °C. The concentration of dye (ca. 10^{-5} M) was always much lower than that of NaOH. Reaction was started by addition of a small volume of a water solution containing the dye to mixtures already containing all other components. Before data acquisition, the mixtures were shaken vigorously until a transparent solution was achieved.

¹H NMR spectra of microemulsion water were recorded on a Bruker WM 250 spectrometer operating at 250 MHz. Experiments were carried out using a concentric capillary containing DMSO-*d*₆ (Aldrich) whose residual proton signal was used as an external standard for chemical shift measurements. The instrument was field locked on the deuterium resonance.

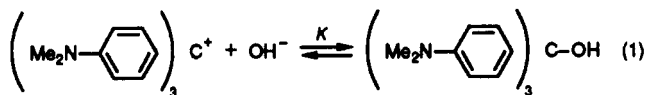
Results and Discussion

Alkaline fading of CV was studied in a wide range of microemulsion compositions. The change in absorbance at 590 nm with time showed a surprising behavior in every case. Initially, the absorbance decreases exponentially as expected for the normal hydrolysis leading to the final product (colorless alcohol). However, after some time, the absorbance begins to increase slowly, until, typically after 24–36 h, the visible spectrum of the reaction mixture is exactly the initial one; that is, the initial concentration of CV has been recovered. This phenomenon is completely reproducible and was observed under all experimental conditions investigated. This pattern of behavior results in atypical absorbance-time profiles; the absorbance decays initially, passes through a minimum, and increases again until reaching its initial value. The minimum absorbance observed depends on the experimental conditions (OH[−] concentration and microemulsion composition). Figure 1 shows a typical example of the evolution



of absorbance with time.

Our explanation for this unusual behavior, relies on the fact that crystal violet hydrolysis is a reversible reaction



whose equilibrium constant in water ($K = 4 \times 10^4 \text{ M}^{-1}$) has been measured by Ritchie and co-workers.²¹ The high value of K means that, under typical OH[−] concentrations ($>10^{-3}$ M), the equilibrium strongly favors the carbinol and the remaining concentration of CV is undetectable. On the other hand, we must keep in mind that our system also contains AOT, a molecule susceptible to hydrolysis with consumption of base.^{22,23} Scheme I shows the resulting situation if we include this process in our kinetic scheme.

The key feature of this scheme is the fact that the disappearance of OH[−] due to AOT hydrolysis will result in a shift of equilibrium 1 to the left. It is important to note that, although hydrolysis of AOT is a slow process,²² the fact that the AOT concentration lies in the range 0.1–0.6 M, whereas the OH[−] concentration—both referred to the total volume—is typically ca. 10^{-2} – 10^{-3} M, means that small percentages of hydrolysis (less than 5%) result in an important reduction in the OH[−] concentration and can therefore induce a shift to the left of the equilibrium, that is, toward recovery of CV. An additional factor leading to the observed behavior can be a change in the K value in our systems compared with that measured in water. Bunton and co-workers⁸ have detected changes in the equilibrium constants of related equilibria in normal micelles.

A further test to our explanation of this unusual phenomenon came when studying the same reaction with the related carbocation malachite green. The absence of one of the N(CH₃)₂ in one of the aromatic rings causes a strong change in the value of K in water ($K = 1.2 \times 10^7 \text{ M}^{-1}$),²¹ which becomes 300 times larger than in the case of CV. This difference in K means that the reduction in the OH[−] concentration due to hydrolysis of AOT must be 300 times larger than in the case of CV for the recovery of the dye to be observed. This proved to be the case. The green color steadily disappears with time following an exponential decay, no further recovery of color being observed for months.

Our results for the alkaline fading of CV in microemulsions show that the first step (hydrolysis of the dye) takes place usually in a shorter time scale than that of the second process (hydrolysis of the surfactant). However, this complex behavior makes the kinetic analysis of our data more difficult and reduces the confidence that can be

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Table I. Representative Experimental Pseudo-First-Order Rate Constants (k_0), Effective OH^- Concentration in the Water Pools ($[\text{OH}^-]_w$), and Calculated Bimolecular Rate Constants (k_2) for the Alkaline Fading of CV and MG at Different Microemulsion Compositions ($[\text{OH}^-] = 5 \times 10^{-3} \text{ M}$ (referred to total volume))

w	[AOT]/M	$[\text{OH}^-]_w/\text{M}$	$10^4 k_0/\text{s}^{-1}$	$10^2 k_2/(\text{M}^{-1} \text{s}^{-1})$
Crystal Violet				
6	0.33	0.13	0.66	0.049
8	0.33	0.107	0.73	0.068
10	0.33	0.083	9.8	1.2
12	0.33	0.068	9.0	1.3
14	0.33	0.060	7.9	1.3
16	0.33	0.052	7.4	1.4
18	0.33	0.046	6.1	1.3
20	0.33	0.042	5.4	1.3
22	0.33	0.0375	4.9	1.3
24	0.33	0.035	4.8	1.4
26	0.33	0.032	4.2	1.3
28	0.33	0.030	3.8	1.3
30	0.33	0.026	3.3	1.3
30	0.4	0.023	3.0	1.3
30	0.5	0.018	2.3	1.2
30	0.17	0.051	4.1	0.8
Malachite Green				
8	0.33	0.1	4.4	0.44
12	0.33	0.068	5.3	0.78
20	0.33	0.042	8.5	2.1
28	0.33	0.03	7.4	2.5
20	0.4	0.035	8.4	2.4
20	0.5	0.028	7.2	2.6

placed upon the rate constants obtained from the analysis of the first part of the kinetic curves. In particular, the possibility that the concentration of OH^- may change during this first period would result in a deviation of the system from pseudo-first-order conditions. An additional problem is related to the possibility that changes in K may cause the reversibility of eq 1 to be significant under our conditions. In such a case the observed rate constants would contain contributions from both the forward and reverse processes.

Keeping this in mind, we have analyzed the first part of the absorbance-time curves. The experimental data for early stages of the reaction showed an acceptable fit to the exponential equation to be expected for a pseudo-first-order process. It is worth noting that, in some cases, especially when w is low ($w < 10$), reaction rates are so slow that interference from AOT hydrolysis is appreciable already in very early stages of the reaction; to avoid this, rate constants in this case were obtained by the initial rate method. Table I summarizes the values of the pseudo-first-order rate constants k_0 obtained under different experimental conditions. Together with the concentration of the microemulsion components, referred to the total volume of solution, Table I also shows the value of $w = [\text{H}_2\text{O}]/[\text{AOT}]$. This ratio seems to be a parameter with a great influence upon the structure of the microemulsions, since it determines the size of the water pools,^{20,24} as well as the physical properties of the entrapped water.^{20,25-30} Figure 2 shows the variation of k_0 with w for fixed concentrations of AOT and OH^- . The reaction rate is

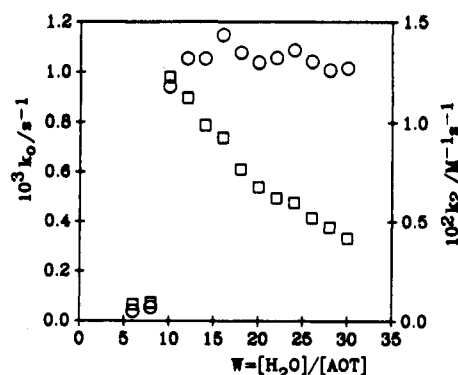


Figure 2. Experimental pseudo-first-order rate constants k_0 (\square) and calculated bimolecular rate constants k_2 (\circ) for alkaline fading of CV plotted vs the water/AOT mole ratio w . $[\text{AOT}] = 0.33 \text{ M}$, and $[\text{NaOH}] = 5 \times 10^{-3} \text{ M}$.

very low at $w < 10$, rises abruptly at $w = \text{ca. } 10$, and then decreases gradually with increasing w .

An interpretation of the observed experimental behavior requires knowledge of the location of both reagents in the microemulsion. Whereas OH^- ions must reside in the aqueous pseudophase of the microemulsion, electrostatic attraction between CV and AOT head groups will tend to locate the dye close to the interface. It can be located either in a water-rich environment, that is, in the interfacial layer of the water pool, or anchored in the surfactant layer without significantly protruding to the water pool. To further investigate this point, we performed a study on the influence of the presence of CV upon the NMR signal of water protons in microemulsions. Working at 0.05 M AOT at $w = 5$, the observed chemical shift of the water proton resonance was 0.23 ppm upfield in the presence of $1.6 \times 10^{-4} \text{ M}$ CV (referred to the total volume of solution). Regular upfield shifts were observed at several w values (0.21 ppm at $w = 10$ and 0.1 ppm at $w = 20$). These results strongly point to a close interaction between the dye and the water molecules in the pool. The magnitude of the shift decreases as w increases, as expected from a reduction in the relative number of water molecules perturbed by CV as the size of the water pool increases. We can therefore conclude that CV also resides in the water pools, probably close to the interfacial layer, in a location similar to that proposed for the aromatic dication methylviologen.³¹

Reaction between CV and OH^- will therefore take place in the aqueous microdroplets, the observed rate constants depending on both the "true" bimolecular rate constant and the effective concentration of OH^- ions around CV. The simplest model we can think of assumes a homogeneous distribution of OH^- ions in the aqueous pseudophase, including the region occupied by CV. This assumption is, probably, an oversimplification, since electrostatic repulsion between OH^- and AOT head groups probably concentrates the hydroxyl ions in the core of the microdroplets.³² According to this simple model, we have estimated in each case the effective concentration of OH^- in the aqueous phase and, from this, the true bimolecular rate constant in the aqueous microdroplets. The results of this procedure are shown in the last column of Table I. Figure 2 also shows the values of this bimolecular rate constant k_2 for different values of w .

The table shows a reasonable constancy in the values of k_2 which, under most experimental conditions, lie in

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(32) As pointed out by one reviewer, the assumption of a uniform distribution of OH^- in the water pseudophase may be reasonable in view of the high ionic concentration in the water droplets.

the range $(0.8\text{--}1.4) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. This range of values is in reasonable agreement with values in the range $(1.5\text{--}2.5) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ found by Izquierdo et al.¹⁷ when studying the same reaction at 30 °C in water/AOT/heptane microemulsions. It is important to note, however, the significant deviation of values corresponding to experiments with low w . This fact can be appreciated in Figure 2, which shows the constancy of k_2 in the case of $w > 10$, but the abnormally low reactivity found for microemulsions with very low w . Some studies¹⁶ even suggested the absence of reaction for $w < 5$. A possible explanation for these anomalies arises when we consider the size of the aqueous microdroplets, whose radius obtained from small angle neutron scattering experiments is a direct function of w ($r = 1.5w$).³³ At $w < 8$, for example, the radius does not exceed 12 Å. Such microdroplets are not able to accommodate our reagents in an "easy way". CV is a molecule with a slight deformation from planarity;³⁴ simple models predict for this carbocation a radius of about 4–5 Å. Therefore, introduction of this molecule in a water pool of low w will cause structural perturbations in the microemulsion. One could argue that the location of this large molecule in the water pools probably results in a polydispersity in sizes, so that microdroplets containing CV become larger than those which are vacant, in analogy with the more studied case of the solubilization of proteins in microemulsions of low w .³¹ This phenomenon could be accompanied by the "exclusion" of OH⁻ from these "filled" microdroplets, where less water would be available for hydrogen-bonding solvation of OH⁻. This reduction of the OH⁻ concentration would explain the observed reduction in reactivity.

We must still explain why the mean value for the true bimolecular rate constant found in "normal" microemulsions ($w > 10$) is only $1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, compared with the value of 0.15 that we have found for the reaction in water, in agreement with literature values.²¹ There are important differences between surfactant-entrapped water and bulk water, and some of them may have kinetic consequences. Microemulsion water has a high ionic strength, which can be estimated³⁵ to be between 2 and 9 M, depending on the microemulsion composition, a fact that can be important since we are studying a reaction in which both reagents bear electrical charge. Additionally, some researchers have speculated about changes in the polarity or dielectric constant of microemulsion water with respect to normal water.³⁶ These considerations led us to investigate the influence of the dielectric constant and ionic strength upon the alkaline fading of CV in homogeneous media.

In agreement with predictions from simple electrostatic theories,³⁷ we found that the alkaline fading of CV in water was accelerated by the presence of organic cosolvents such as dioxane. Therefore, we cannot attribute the decrease in reactivity observed in microemulsions to the lower polarity of microemulsion water with respect to normal water. Table II shows the effect of ionic strength upon the reaction rate. Increasing the NaCl concentration causes a reduction in the reaction rate; at 1.5 M NaCl, for example, a reduction of 50% in the reaction rate is observed. The existence of a high ionic strength in the aqueous pseudophase of microemulsions could therefore

Table II. Influence of Ionic Strength on the Alkaline Fading of Crystal Violet in Water ([NaOH] = 0.15 M)

[NaClO ₄]/M	k_0/s^{-1}	[NaCl]/M	k_0/s^{-1}
	2.00×10^{-2}		2.00×10^{-2}
0.023	7.73×10^{-3}	0.0201	1.96×10^{-2}
0.058	2.56×10^{-3}	0.081	1.82×10^{-2}
0.093	1.26×10^{-3}	0.121	1.73×10^{-2}
0.14	8.69×10^{-4}	0.20	1.56×10^{-2}
0.58	2.29×10^{-4}	0.51	1.22×10^{-2}
1.17	5.61×10^{-5}	1.47	1.02×10^{-2}

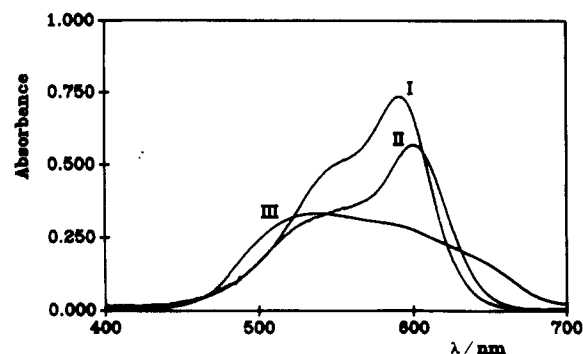


Figure 3. Crystal violet spectrum (I) in water, (II) in a water/AOT/isooctane microemulsion [AOT] = 0.3 M, $w = 5$, and (III) in a 0.22 M aqueous solution of NaClO₄. [CV] = $8.37 \times 10^{-6} \text{ M}$.

Table III. Ratio between the Intensities of Bands A and B (see text) of the Visible Spectrum of CV in Different Media

medium	$R = I_A/I_B$	medium	$R = I_A/I_B$
water	1.43	0.06 M NaClO ₄	1.03
microemulsion, $w = 5$	1.67	0.11 M NaClO ₄	0.96
microemulsion, $w = 10$	1.62	0.18 M NaClO ₄	0.87
microemulsion, $w = 23$	1.58	0.23 M NaClO ₄	0.86
microemulsion, $w = 35$	1.51	0.29 M NaClO ₄	0.84

be considered responsible for the reduction in reactivity observed. However, extrapolation of the data may not be so simple. Table II also shows the influence of ionic strength when NaClO₄ is used. In this case, inhibition is much more marked and reaches a reduction of 400 times in the reaction rate at 1.2 M NaClO₄, suggesting a specific inhibition by perchlorate ions. This specific behavior might be due to some specific interaction between CV and ClO₄⁻, and this notion led us to look for spectral evidence of such an interaction.

The visible spectrum of CV in water (Figure 3) consists of a strong peak at 590 nm (band A) and a shoulder (band B) at 540 nm. The existence of two bands has been attributed to the "propeller-shaped" structure of CV and the existence of two isomers in solution: a symmetrical helical isomer (band A) and a distorted helical isomer (band B).³⁴ The relative height A/B measured in water is 1.48 and seems to be solvent-dependent.³⁴ Table III shows the ratio of heights A/B under different experimental conditions. When the spectrum is recorded in the presence of NaClO₄ (Figure 3), the heights of both bands strongly change and the ratio A/B becomes 0.84; i.e., an inversion in the relative heights of bands A and B is observed (Table III). Shifts in the position of both bands are also observed. The spectral change is so strong that one can visually appreciate variations in the intensity and shade of the color when perchlorate ions are present. This piece of evidence strongly points toward a strong stabilizing association between the carbocation and ClO₄⁻, probably in the form of ion pairs. Formation of ion pairs probably affects the relative stability of the two isomers of CV, and undoubtedly affects chemical reactivity, therefore explaining the anomalous inhibition caused by ClO₄⁻ upon

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the alkaline fading of CV.³⁸ There is evidence in the literature of the existence of specific interactions between structurally related carbocations and counterions.³⁹⁻⁴²

Table III also summarizes some spectral information about the characteristics of CV in microemulsions of typical composition (Figure 3). Incorporation of the dye to the microemulsions also induces some changes in its visible spectrum, in agreement with Rodenas et al.'s¹⁴ observations in water/cetyltrimethylammonium bromide/1-hexanol microemulsions. These modifications could reflect a change in the polarity of the molecular environment, but also some specific interaction between CV and the surfactant head groups. This latter phenomenon could be responsible for an additional reduction in the reaction rate with respect to that measured in water, which—as

(38) If we assume only free CV is susceptible to attack by OH⁻, it is possible to estimate from our kinetic data the equilibrium constant for formation of ion pairs K_{ip} . We have fitted our experimental data to the equation $k_{\text{eff}} = k_2[\text{OH}^-]/(1 + K_{ip}[\text{ClO}_4^-])$ after correcting the experimental k_{eff} values to zero ionic strength by means of the data obtained for NaCl inhibition. We obtained for K_{ip} a value of 160 M^{-1} , indicative of a strong association between CV and perchlorate ions.

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suggested by one reviewer—could be especially important in the case of microemulsions with very low water content.

An additional factor leading to the observed low reactivity of the reagents entrapped in the microemulsion water pools could be an enhanced steric hindrance with respect to the situation in free water.¹⁷ Preferential location of CV in the neighborhood of AOT head groups—probably in a situation of restricted mobility—can hinder the formation of a normal transition state with respect to the situation in free water.⁴³

Finally, Table I also lists some of the results of experiments carried out with MG in our microemulsions. Again, except for the unusual slowness of the reactions at low w ($w = 8$ and, to a lesser extent, $w = 12$), the calculated bimolecular rate constants are effectively constant, with a mean value of ca. $2.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, some 60 times lower than the corresponding value in water, $1.46 \text{ M}^{-1} \text{ s}^{-1}$.

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