Kinetics and Catalysis, Vol. 46, No. 3, 2005, pp. 364–367. Translated from Kinetika i Kataliz, Vol. 46, No. 3, 2005, pp. 390–393.

Influence of Micelles of Different Types of Surfactant on the Mechanism of Diphenylamine Oxidation with Potassium Persulfate

M. G. Gevorkyan

Yerevan State University, Yerevan, 375049 Armenia

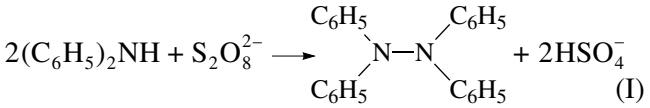
Received February 16, 2004

Abstract—Data on diphenylamine oxidation with potassium persulfate in aqueous–organic micellar solutions of different surfactants are generalized. The general effects of different surfactants are explained by the fact that different parts of micelles influence particular steps of multistep chemical reactions. This approach will enable one to control the formation rates of the intermediate or final product by making use of reaction specificity.

Earlier, we studied the kinetics and mechanism of the oxidation of the oil-soluble compound diphenylamine (DPA) with the water-soluble oxidant potassium persulfate (PPS) in homogeneous aqueous–organic media (containing 50% ethanol, 33% dioxane, or 45% acetone) with a fixed dielectric constant of $\varepsilon = 49$. This reaction was shown to be free-radical, nonchain, and stepwise, regardless of the nature of the organic solvent [1].

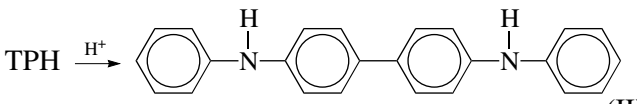
At low reactant concentrations (~5×10^{-3} mol/l, pH ~ 7, $T \sim 300$ K), the main reaction product is diphenylbenzidine violet (DPBV). Its formation in water–ethanol homogeneous media can be described by a three-step mechanism [1].

In the first step, DPA is oxidized with persulfate ($S_2O_8^{2-}$ anion) into tetraphenylhydrazine (TPH) via the following stoichiometric reaction:



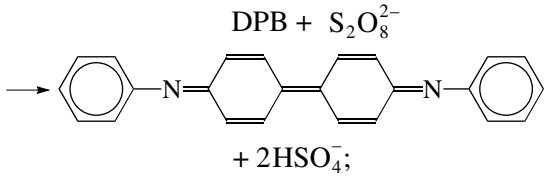
(I)

In the second step, TPH undergoes a rapid benzidine rearrangement into diphenylbenzidine (DPB) under the catalytic action of H^+ ions of acids (for example, HSO_4^-, which is one of the reaction products):



(II)

In the third step, DPB is oxidized by another $S_2O_8^{2-}$ anion to form dark violet DPBV:



(III)

DPB is oxidized with persulfate at a higher rate than the starting amine. In water–ethanol solutions, the initial rates of the DPA + PPS reaction determined from PPS consumption (iodometric data) and from the accumulation of the final product of DPA oxidation (DPBV) (colorimetric D data at $\lambda = 440$ nm) are described by the same second-order equation: $w_0 = k[\mathrm{PPS}]_0[\mathrm{DPA}]_0$. This suggests that the slowest step determining the rate of the above system of consecutive reactions is reaction (I). DPA oxidation with persulfate was studied in micellar solutions of the anionic surfactant $C_{15}H_{31}SO_3Na$ (E-30) [2, 3], the nonionic surfactants $C_{16}H_{33}(CH_2CH_2O)_{20}OH$ (OS-20) and $C_{17}H_{35}(CH_2CH_2O)_{30}OH$ (Ts-30) [4], and the cationic surfactant $[C_{12}H_{25}N(CH_3)_3]Cl$ (DTAC) [5].

Knowing the nature of the reacting species, one can expect that, in the presence of different micelles, the reactants will be redistributed among discrete zones of the reaction system owing to hydrophobic and electrostatic interactions. Persulfate anions will be distributed between the aqueous phase and the micellar surface, being repelled by anionic micelles and attracted by cationic micelles. Taking into account that the DPA + PPS reaction is consecutive, we spectrophotometrically determined the zone of localization of DPA and TPH (the oxidation product) in micelles [6]. Based on the data obtained in that study, we concluded that, in micellar solutions of three types of surfactant (E-30, OS-20, and DTAC), the NH group of the DPA molecule is in

0023-1584/05/4603-0364 © 2005 MAIK "Nauka/Interperiodica"

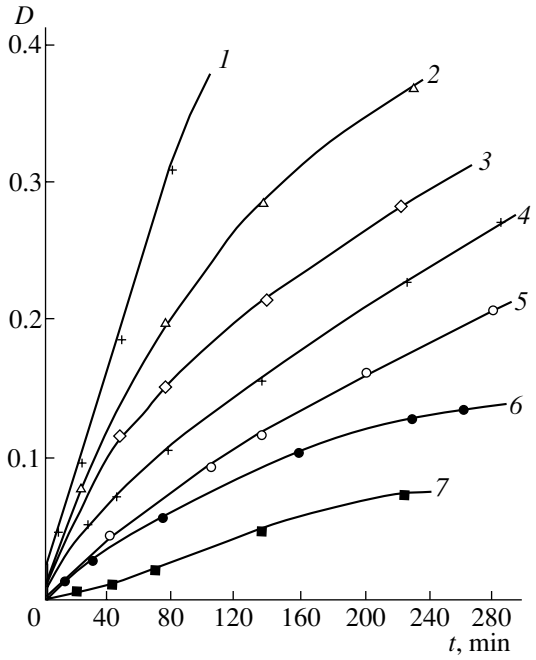


Fig. 1. Kinetics of accumulation of the product of the DPA + PPS reaction in water–dioxane solutions in the presence of E-30. [E-30] × 10^2 = (*1*) 0, (*2*) 0.96, (*3*) 1.9, (*4*) 3.2, (*5*) 6.4, (*6*) 9.6, and (*7*) 30 mol/l; $[DPA]_0 = [PPS]_0 = 5 \times 10^{-3}$ mol/l; λ = 440 nm; *T* = 298 K.

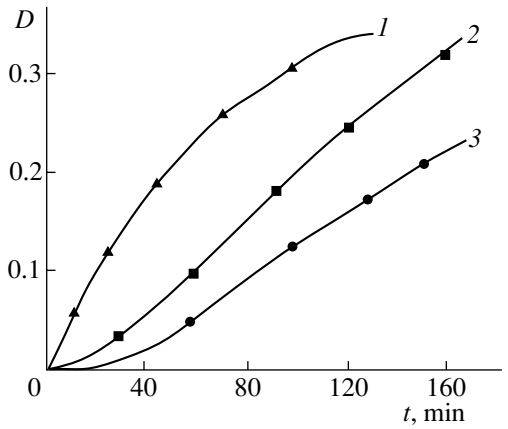


Fig. 2. Kinetics of accumulation of the product of the DPA + PPS reaction in water–ethanol media in the presence of OS-20. [OS-20] × 10^2 = (*1*) 2.67, (*2*) 5.35, and (*3*) 7.1 mol/l; $[DPA]_0 = [PPS]_0 = 5 \times 10^{-3}$ mol/l; λ = 440 nm; *T* = 308 K.

the polar environment, while the TPH molecule is in the nonpolar medium; that is, DPA and TPH are located in different regions of the micelles, regardless of the nature of the polar group of the surfactant.

In molecularly organized solutions of anionic [2, 3] and nonionic [4] surfactants (Surf), small additives of micelles were found to decrease the rate of PPS consumption and the formation rate of the colored reaction product (DPBV), no matter what the organic cosolvent. The plot of the DPBV accumulation rate in the presence of the cationic surfactant DTAC versus DPBV concentration has a well-defined maximum at $[Surf]_{opt} = 9.1 \times 10^{-3}$ mol/l [5].

In this work, we attempt to explain the general effects of molecularly organized systems of different surfactants in terms of the specific action of different parts of micelles on particular reaction steps, without considering the kinetics of each step in detail.

Note that the polar and nonpolar parts of micelles are involved in noncovalent interactions different in nature and, accordingly, exert independent effects on the reaction that occurs in their medium. Owing to the same noncovalent interactions, the polar and nonpolar parts of surfactant molecules act independently on the water surface, according to Langmuir's principle. The nonpolar core of all types of surfactant hydrophobically binds TPH, bringing it from the reaction zone to the nonpolar medium and thereby screening it from the $S_2O_8^{2-}$ and H^+ ions. In other words, spatial separation of TPH from PPS and H^+ takes place in micellar matrices owing to hydrophobic interactions. The retarding effect of the surfactant on the DPA + PPS reaction can be due to not only this separation of the reactants but also the unfavorable influence of the microenvironment of the surfactant micelle cores on the benzidine rearrangement of TPH [7]. At a certain concentration of micelles of the anionic (E-30) [2, 3] or nonionic surfactant (OS-20, Ts-30) [4], this effect prevents further TPH transformations and the reaction ends in TPH formation (reaction (I)), which is an intermediate step in the micelle-free system (Figs. 1, 2). This explains both the retardation of the reaction in question (at low micelle concentrations) and the change in reaction stoichiometry (at high surfactant concentrations). To study the kinetic effect of TPH solubilization by the micelle core, the reaction was carried out in the presence of micelles presaturated with TPH [8]. It was found that the product formation curves for TPH-saturated micelles of both OS-20 and E-30 lie between the curves for the micelle-free systems and the curves for systems containing so-called "empty" (TPH-free) micelles.

Due to electrostatic or ion–dipole interactions, the polar part of the micelles differently affects (increases or decreases) the local concentrations of persulfate anions and protons on the micelle surface, which is the main reaction zone. It is this redistribution of the reactants between different zones of the micellar matrix that is responsible for the observed changes in the rates of reaction steps.

In the presence of the nonionic surfactants OS-20 and Ts-30, which are hydroxyethylated alcohols with very similar hydrocarbon radicals and hydroxyethylated chains of different lengths, the decrement in both potassium persulfate consumption and DPBV forma-

tion rates increases with increasing surfactant concentration [4]. Note that, at [OS-20] = 2.67×10^{-2} mol/l, the reaction mixture first turns yellow, indicating TPH accumulation. A violet shade characteristic of the final product (DPBV) appears no sooner than in ~60 min. The difference in color between the DPA oxidation products makes it possible to directly (visually) determine whether the reaction is terminated at an intermediate step (TPH formation) or proceeds further. At [OS-20] $\geq 5.3 \times 10^{-2}$ mol/l, the reaction yields only TPH, which undergoes no further oxidation. In this case, a smaller number of moles of PPS is consumed per mole of DPA. Induction periods appear in the optical density–time (D–t) curves, lengthening as the surfactant concentration is increased. The TPH formation rate in the presence of OS-20 (5.3×10^{-2} mol/l) is related to reactant concentration as

$$\frac{d[TPH]}{dt} = k'([PPS]_0 - x)([DPA]_0 - 2x).$$

In water–ethanol DPA + PPS reaction mixtures containing nearly equal molar concentrations of nonionic surfactants, the inhibition effect of OS-20 is stronger than that of Ts-30. For example, at [OS-20] = 5.3×10^{-2} mol/l, the reaction is terminated at the stage of TPH formation, whereas some amount of DPBV is formed at [Ts-30] = 5.8×10^{-2} mol/l. Note that a similar behavior is shown by the PPS consumption rate in these systems [4].

Thus, the longer the hydroxyethylated chain in the nonionic surfactant molecule, the weaker the inhibition effect of the micelles. These results can be due to PPS reacting with the hydroxyethylated chain of the nonionic surfactant. Our data [9, 10] indicate that PPS decomposition in aqueous solutions of hydroxyethylated alcohols is due to reactions that are initiated by the thermal decomposition of PPS and are accompanied by the degradation of the hydroxyethylated chain.

In the case of DTAC, the DPA molecules and $S_2O_8^{2-}$ anions are localized in the same reaction zone, specifically, on the positively charged micelle surface [5]. This increases the rate of step (I) in a certain surfactant concentration range ($C < C_{opt}$). However, as TPH is accumulated, it appears in the hydrophobic micelle core to slow down the reaction. As the DTAC concentration is further raised, the reaction rate falls, as in the case of the anionic and nonionic surfactants (see above). As a consequence, the rate of the reaction in the cationic micelle medium passes through a well-defined maximum. The decrease in the DPA + PPS reaction rate at [DTAC] > $[Surf]_{opt}$ is caused by the increase in the micellar volume (which results in a decrease in the reactant concentration in the reaction zone, as follows from the theory of micellar catalysis [11]) and by the hydrophobic binding of TPH by the micelle core. Furthermore, the H^+ ion deficiency near the cationic micelle surface prevents the benzidine rearrangement and subsequent reaction steps. Evidently, the dual influence of the cationic micelles on the DPA + PPS reaction rate (acceleration of the steps involving $S_2O_8^{2-}$ and deceleration of the steps involving H^+) favors TPH accumulation, thus enhancing the selectivity of the reaction toward the intermediate reaction product.

To elucidate the role of the benzidine rearrangement in the reaction in question, we studied the effect of H_2SO_4 additives in water–dioxane solutions of E-30 [12]. It was demonstrated that, at [E-30] = 6.4×10^{-2} mol/l, 0.34–0.9 M H_2SO_4 exerts no considerable effect on the initial reaction rate and causes an increase in reaction rate only after ~160 min. Since in micelle-free systems acid additives have no direct effect on the DPA + PPS reaction rate [1] because diphenylamine is a weak base ($pK_a = 13.15$) incapable of any considerable salt formation, our results can be explained by the protonation of TPH (by analogy with the monoprotonation and diprotonation of 1,2-diphenylhydrazine under the action of HCl in the absence [13] or presence [7] of anionic micelles). It is believed that TPH molecules gain a charge through monoprotonation or diprotonation and escape from the nonpolar micelle core to a zone accessible for $S_2O_8^{2-}$ (or do not enter the core) to enhance the selectivity of the reaction towards the final product.

The kinetics and mechanism of the DPA + PPS reaction in water–ethanol solutions were studied in wide ranges of E-30 micelle and HCl concentrations (≤0.1 and ≤1.6 mol/l, respectively) at 303 K [14]. HCl concentration was varied at [E-30] = const = 6.65×10^{-2} and 4.75×10^{-2} mol/l, and E-30 concentration was varied at [HCl] = const = 0.875 and 0.625 mol/l. As already mentioned, in the absence of micelles at $[H^+] \cong [PPS]_0 = [DPA]_0$, acid additives exert no effect on the rate of DPA oxidation with persulfate. At the same time, HCl concentrations exceeding the DPA and PPS concentrations by a factor of ~250 cause some decrease in the DPA + PPS reaction rate (Fig. 3, curves *1*, *2*). This effect is apparently due to the $S_2O_8^{2-} + H^+$ reaction yielding $HS_2O_8^-$, which shows only a low reactivity toward DPA.

As HCl is introduced into a DPA + PPS reaction system containing a fixed E-30 concentration (6.65×10^{-2} mol/l), the reaction rate changes in a complicated way (Fig. 3). In the presence of [E-30] = 6.65×10^{-2} mol/l and in the absence of HCl, the reaction rate decreases (Fig. 3, curve *5*). At low HCl concentrations (≤0.225 mol/l), the reaction rate at [E-30] = const decreases to a greater extent (curve *6*). However, at [HCl] ≥ 0.625 mol/l, the rate curves are *S*-like: for instance, curve *4* lies below curves *5* and *6* up to ~130 min after the reaction onset and above these curves starting at ~160 min.

The plot of the optical density of the reaction mixture at t = 300 min (D_{300}) as a function of E-30 concentration ([HCl] = const) in the region of low E-30 concentrations ([E-30] < 1×10^{-2} mol/l) is a bell-shaped

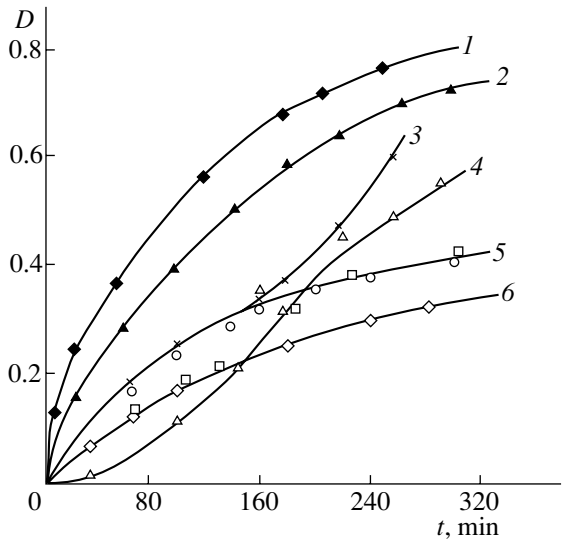


Fig. 3. Time dependence of the optical density of DPA + PPS reaction mixtures in aqueous ethanol in the (*1*, *2*) absence and (*3*–*6*) presence of E-30 (6.65×10^{-2} mol/l) at [HCl] = (*1*) 0, (*2*) 1.374, (*3*) 0.875, (*4*) 0.625, (*5*) 0, and (*6*) 0.225 mol/l; λ = 440 nm; T = 303 K.

curve typical of micellar catalysis. At higher concentrations ([E-30] $\geq 2 \times 10^{-2}$ mol/l and [HCl] $\geq$ 0.625 mol/l), the rate of step (II) is somewhat lower than that in the absence of additives, and the colorimetrically determined reaction rate remains virtually unchanged as [E-30] is increased [14]. Evidently, under these conditions, the inhibiting effect of the micelles is partially compensated for by the accelerating effect of the acid.

The above data led us to conclude that benzidine rearrangement is the key process, making it possible to change the nature of noncovalent interaction between the micellar matrix and the reactants by varying $[H^+]$. This is a way of controlling the selectivity of the multistep oxidation of DPA towards the intermediate or final product in the molecularly organized system.

The oxidation of aromatic amines has attracted special interest in recent years because the products of oxidative polymerization of aromatic amines and their copolymers [15, 16] in aqueous and nonaqueous media, which are conducting polymers with conjugated bonds, show promise for a variety of applications, including antistatic coatings, solar batteries, and electronic devices. The selective effect of different types of surfactant in the presence of electrolytes on certain steps of DPA oxidation with persulfate, revealed in our studies, can be used in the oxidative polymerization of diphenylamine [17] and other aromatic amines.

REFERENCES

1. Gevorkyan, M.G., *Extended Abstract of Cand. Sci. (Chem.) Dissertation*, Yerevan: Yerevan Go. Univ., 1970.
2. Gevorkyan, M.G., Beileryan, N.M., and Ashtyan, A.P., *Arm. Khim. Zh.*, 1978, vol. 31, no. 5, p. 291.
3. Gevorgyan, M.G. and Beylerian, N.M., *J. Surf. Sci. Technol.*, 1999, vol. 15, nos. 1–2, p. 90.
4. Gevorkyan, M.G., Karapetyan, T.G., Mar'yanyan, A.I., Levonyan, A.V., and Melkonyan, L.G., *Arm. Khim. Zh.*, 1978, vol. 31, no. 5, p. 296.
5. Gevorkyan, M.G., *Khim. Zh. Arm.*, 2002, vol. 55, no. 3, p. 22.
6. Gevorkyan, M.G., Beileryan, N.M., and Kishoyan, V.S., *Arm. Khim. Zh.*, 1979, vol. 32, no. 5, p. 348.
7. Bunton, C.A. and Rubin, R.J., *Tetrahedron Lett.*, 1975, no. 1, p. 54.
8. Gevorkyan, M.G., *Uch. Zap. Yerevan. Gos. Univ.*, 2004, no. 1, p. 59.
9. Gevorkyan, M.G., Nalbandyan, Dzh.M., and Beileryan, N.M., *Arm. Khim. Zh.*, 1979, no. 7, p. 505.
10. Gevorgyan, M.G., Nalbandyan, J.M., and Beyleryan, N.M., *Oxid. Commun.*, 2004, vol. 27, no. 2, p. 284.
11. Berezin, I.V., Martinek, K., and Yatsimirskii, A.K., *Usp. Khim.*, 1973, vol. 42, no. 10, p. 1729.
12. Gevorkyan, M.G., Yavryan, S.Sh., and Beileryan, N.M., *Uch. Zap. Yerevan. Gos. Univ.*, 2001, no. 1, p. 65.
13. Bunton, C.A. and Rubin, R.J., *Tetrahedron Lett.*, 1975, no. 1, p. 59.
14. Gevorkyan, M.G., *Khim. Zh. Arm.*, 2003, vol. 56, no. 4, p. 5.
15. Athawale, A.A., Patil, S.F., and Deore, B., *Polymer*, 1999, vol. 40, no. 17, p. 4929.
16. Chung, Ch.-Y., Wen, T.-Ch., and Gopalan, A., *Electrochim. Acta*, 2001, vol. 47, no. 3, p. 423.
17. Elothamani, D., Guiliantion, G., and Simonet, J., *Eur. Polym. J.*, 1996, vol. 32, no. 1, p. 1.