ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 5, pp. 903–907. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © S.Yu. Doronin, R.K. Chernova, A.A. Burmistrova, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 5, pp. 761–765.

Effect of the Micellar Surfactant Nanoreactors on the Reactions of 2,4-Dinitrophenylhydrazine with Some Aldehydes

S. Yu. Doronin, R. K. Chernova, and A. A. Burmistrova

Chernyshevskii Saratov State University, Chemical Faculty,
Astrakhanskaya 83, building 1, Saratov, 410012 Russia
e-mail: DoroninSU@mail.ru

Received July 31, 2007

Abstract—By thermogravimetry, the IR and electronic spectroscopy physicochemical characteristics of systems including aromatic aldehydes, 2,4-dinitrophenylhydrazine, and a surfactant were investigated. Selective solubilization effect of the cationic surfactant (cetylpyridinium chloride) micelles on the aci-form of hydrazone arising in the alkaline medium was found. The universal character of solubilization by the cationic surfactant micelles in the aromatic aldehyde—2,4-dinitrophenylhydrazine systems was shown by an example of the benzaldehyde derivatives with substituents of different nature. This effect leads to the increase in solubility of the reaction products and the aggregative stability of solutions.

DOI: 10.1134/S1070363208050113

Reaction of 2,4-dinitrophenylhydrazine with carbonyl compounds (aldehydes, ketones, quinones) is widely used in the organic [1–3] and the analytical [4–13] chemistry. Such reactions are distinguished by their high selectivity. The products of these reactions proceeding as a rule in water and organic-water media are the corresponding hydrazones. Under the action of alkali the latter are converted to intensely colored aci-salts **II**.

Effect of the micellar media of surfactants on this type of reactions was not studied before. Considering that the surfactant-based micellar nanoreactors can significantly alter physicochemical properties of systems, the aim of the present work was to establish the effect of various types of surfactants on the reactions of 2,4-dinitrophenylhydrazine with a series of aromatic aldehydes (Table 1).

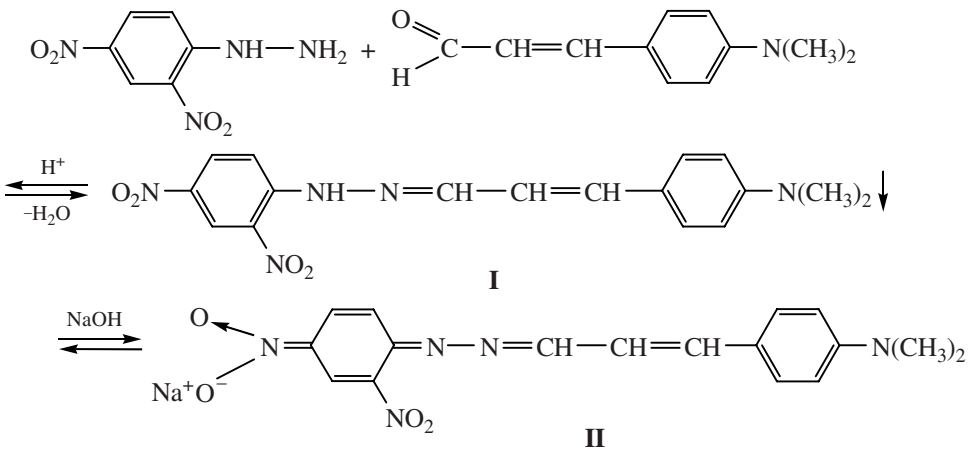
The choice of aldehydes was determined by different position (*o-*, *m-*, *p-*) and the nature of substituents in the aromatic ring with the purpose of evaluating the effect of these factors on the properties of hydrazones formed and their behavior in water and the micellar media.

Effect of various types of surfactants was investigated by an example of model system consisting of 2,4-dinitrophenylhydrazine and *p*-dimethylaminocynnamaldehyde.

As it was shown previously two main reaction steps could be distinguished. In the first stage proceeding in the acidic medium the condensation of reagent with the carbonyl compound takes place to form the poorly water-soluble hydrazone (the electroneutral form **I**). In the second stage proceeding in the alkaline medium the negatively charged aci-form of the corresponding hydrazone is formed and its solubility in water somewhat increases. To prove that the product **I** obtained in the first stage of the reaction is the hydrazone and to evaluate its physicochemical

Table 1. Aromatic aldehydes under investigation

Aldehyde	FW
Benzaldehyde	106.12
p-Dimethylaminobenzaldehyde	149.19
p-Dimethylaminocynnamaldehyde	176.16
p-Methoxybenzaldehyde	136.15
p-Nitrobenzaldehyde	151.13
m-Nitrobenzaldehyde	151.13
p-Chlorobenzaldehyde	186.5
2,4-Disulfobenzaldehyde	262.12



characteristics the substance obtained was isolated in solid state and investigated by thermogravimetry (Fig. 1a), IR spectroscopy (Fig. 1b), and elemental analysis (see Experimental).

The product obtained (Fig. 1a) does not contain the hygroscopic and the structurally-bound water as is confirmed by the broad plateau on the thermogravimetric curve up to 200°C and the absence of the endothermic effect corresponding to the removing of solvent (water) on the differential curve. The sample burns out completely (the mass loss is 100%) and hence does not contain the inorganic admixtures.

Analysis of the IR spectrum of the hydrazone **I** (Fig.1b) showed the presence of the characteristic

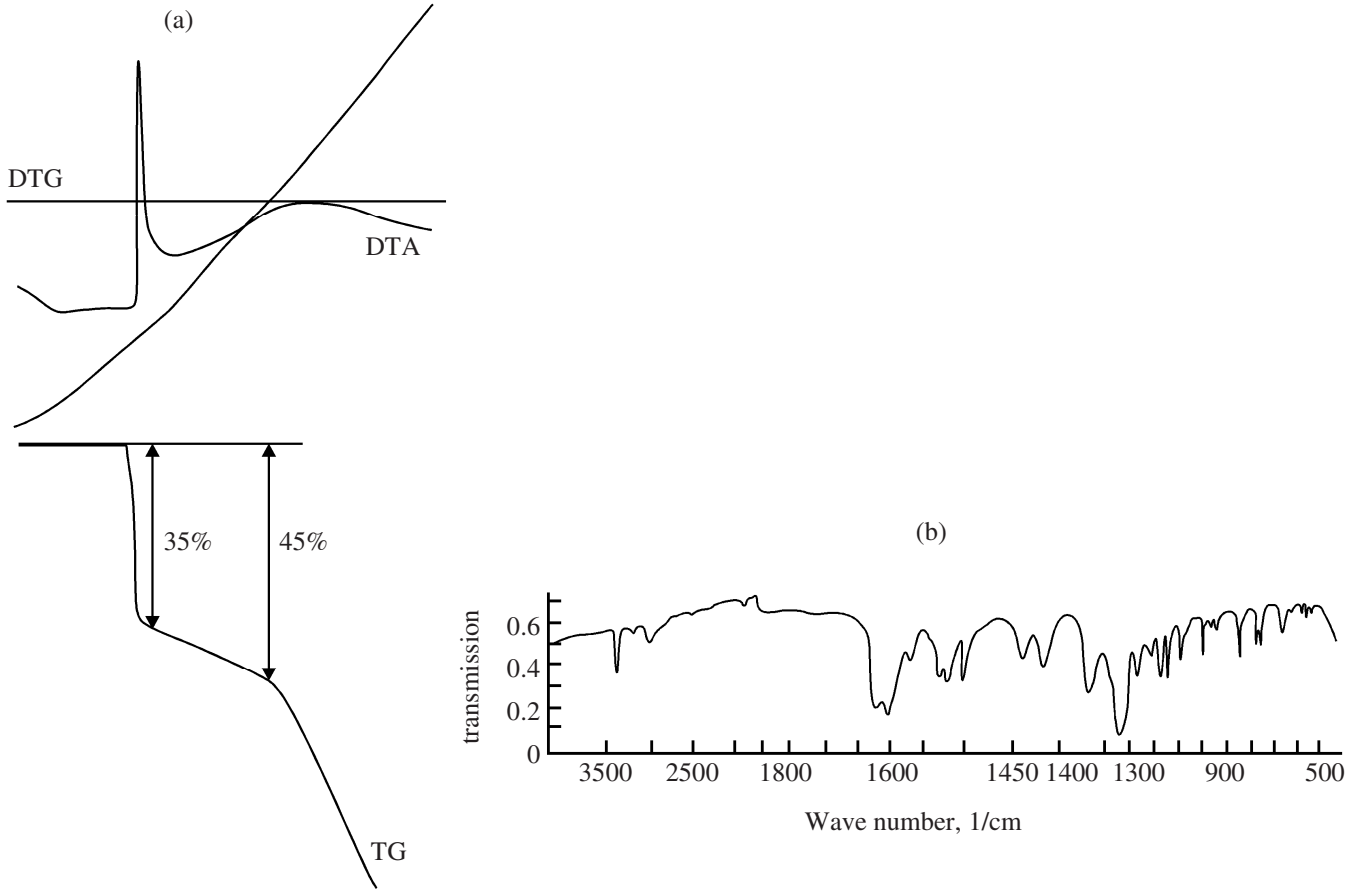


Fig. 1. The thermogram (a) and the IR spectrum (b) of hydrazone **I**.

bands at 1600–1618 cm^{-1} belonging to the azomethine group >C=N–, and also of the band at 3265 cm^{-1} corresponding to the N–H bond vibrations. In the IR spectrum of the hydrazone **I** the absence of bands characteristic of initial reagents was established: at 1715–1695 cm^{-1} (aldehyde group) and at 3200–3500 cm^{-1} (NH_2 group). Hence, the analytical data obtained for the product synthesized confirm that it is hydrazone **I**.

We have studied the reaction of 2,4-dinitrophenylhydrazine with aldehydes in the micelles of surfactants of different nature. Introduction into the system under study of micelles of an anionic surfactant (sodium dodecylsulfate) does alter the reaction character and the properties of hydrazone **I** and of its aci-form **II**. In the micelles of nonionogenic surfactant (OP-10) the insignificant increase in solubility of the form **I** within 5–6 h was observed.

In contrast to the anionic and nonionogenic surfactants the micellar medium of cationic surfactant (cetylpyridinium chloride) provided a complete solubility of the hydrazone aci-form **II**. It seemed expident to evaluate the solubility of hydrazone **I** in the absence and in the presence of micelles of the cationic surfactants (pH 13). The solubility of hydrazone **I** evaluated by the isothermal saturation method was 4.0×10^{-7} mol l^{-1} (7.05×10^{-5} g l^{-1}) in water and 2.5×10^{-5} mol l^{-1} (4.4×10^{-3} g l^{-1}) in the micelles of cetylpyridinium chloride. This finding means that the solubility of hydrazone at the transfer from water to the micellar medium increases ~60 times. Increase in the aggregative stability of solutions was observed (within 5 h). The homogenous solutions obtained were intensely colored (λ_{max} 470–530 nm, Fig. 2) and stable during several hours. Solubilization of the aci-form of hydrazones analogous to **II** occurs evidently in the surface layer of the cationic micelles.

The increase in solubility of hydrophobic substances when the critical concentration of the micelle formation is attained in the solutions of surfactants (the solubilization) in many cases is accompanied by formation of thermodynamically stable isotropic solutions. This process is analogous to extraction. The role of the second phase is played by the micelles of surfactant (pseudophase). The solubilization is affected by different factors like temperature, the nature of surfactant and of the solubilized compound, presence of alien electrolytes, the concentration of counterions, etc. [14]. It is presumable that the sharp increase in the solubility of hydrazone **II** in the micelles of cationic surfactants is governed by two main factors, the electrostatic interaction of the oppositely charged aci-form of hydrazone and the surface of the cationic micelle of surfactant, and the presence of the hydrophobic aromatic rings in compound **II**.

The optimal conditions of the reaction of 2,4-dinitrophenylhydrazine with other aldehydes were also studied. The pH, the concentrations of reagent and of cetylpyridinium chloride, the temperature, and the order of mixing the solutions were varied. It was found that the effect of the cetylpyridinium chloride micelles is independent of the nature and the position of substituent in the aromatic ring of aldehyde under the following conditions: pH 13, C_{DPH} 4×10^{-4} M, C_{CPC} 6×10^{-4}M, t 20–25°C, the order of mixing: dinitrophenylhydrazine–aromatic aldehyde–cetylpyridinium chloride-buffer solution.

Analysis of data listed in Table 2 shows that introduction of the electron-donor [$N(CH_3)_2$, OCH_3] and the electron-acceptor (NO_2, Cl, SO_3H) substituents in the molecule of benzaldehyde practically does not influence such charactristics of the hydrazones obtained as the molar extinction (ε_{mol}), the detection limit and the range of detected concentrations.

Detection limit is determined as the smallest content of a substance which can be found in the

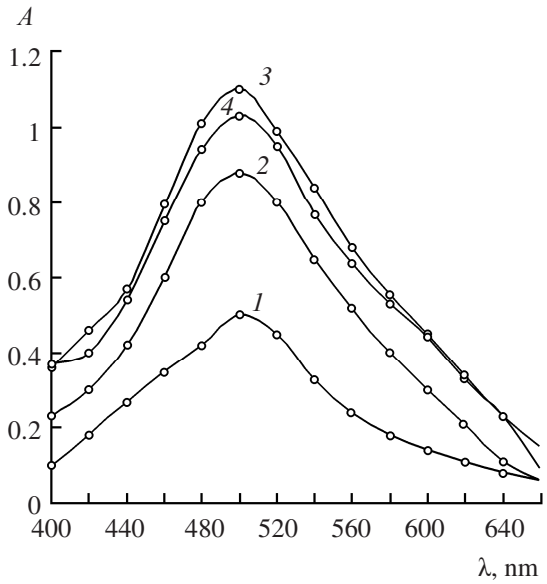


Fig. 2. The electron absorption spectra of the system 2,4-dinitrophenylhydrazine (1×10^{-5} M)–*p*-dimethylaminocynnamaldehyde (1×10^{-5} M)–cetylpyridinium chloride. C_{CPC}: (*1*) 1×10^{-4} M; (*2*) 2×10^{-4} M; (*3*) 6×10^{-4} M; (*4*) 8×10^{-4} M. A reference solution is borate buffer (pH 13), l = 1 cm.

Table 2. Some characteristics of the system aromatic aldehyde–2,4-dinitrophehylhydrazine–cetylpyridinium chloride (pH 13).

Aldehyde	λ_{max}, nm	$\varepsilon_{mol}\times10^4$, $l\ mol^{-1}cm^{-1}$	Detection limit $\times 10^{-6}$, mol l-	Range of detected contents, μg ml^{-1}
p-Dimethylamino cynnamaldehyde	500	12.6	0.39	0.06–0.2
p-Dimethylamino benzaldehyde	480	1.97	1.2	0.18–2.1
Benzaldehyde	470	2.08	2.4	0.25–1.4
p-Methoxybenzaldehyde	470	3.97	1.6	0.28–2.1
p-Nitrobenzaldehyde	530	2.02	1.2	0.18–1.9
m-Nitrobenzaldehyde	470	2.02	1.2	0.18–2.0
p-Chlorobenzaldehyde	470	2.08	1.2	0.20–2.1
2,4-Disulfobenzaldehyde	480	1.87	1.3	0.28–2.3

sample by the given procedure with the given confidential probability. The range of detected concentrations is the range between the smallest and the largest concentration of the given component. For the aci-form of hydrazone of *p*-nitrobenzaldehyde the red shift was observed due to maximum redistribution of the electronic density in the molecule caused by the pronounced induction (*–I*) and mesomeric (*–C*) effects, and also the field effect (*–F*) of the nitro group in p-position of the benzene ring.

Introduction of an electron-donating dimethylamino group and a vinyl fragment in the molecule of benzaldehyde (the case of *p*-dimethylaminocynnamaldehyde) not only increases the conjugation chain in the molecule of the obtained hydrazone by redistribution of the electronic density in the initial aldehyde (a semiquinoid form [15]), but also leads to the 10-fold increase in the ε_{mol} as compared to the other aldehydes under investigation. In [16] quantum chemical calculations were performed on the distribution of the molecular electrostatic potential in the molecules of benzaldehyde and some its derivatives including *p*-dimethylaminobenzaldehyde and *p*-dimethylaminocynnamaldehyde. It was shown that the introduction of dimethylamino group into the molecule of benzaldehyde leads to the alteration in the molecular electrostatic potential in the functional group of aldehydes: An increase was found of the area of negative molecular electrostatic potential around the oxygen atom of the carbonyl group as well as of the positive area of molecular electrostatic potential around the carbonyl carbon atom. Therewith the area of positive values of the molecular electrostatic potential above the carbon atom of the carbonyl group in the *p*-dimethylaminocynnamaldehyde is significantly larger than in the *p*-dimethylaminobenzaldehyde and benzaldehyde.

These electronic effects caused by the dimethylamino group and the vinyl fragment result in the highest reactivity of *p*-dimethylaminocynnamaldehyde among the aromatic aldehydes under study. They also lead to the increase in ε_{mol} of the corresponding hydrazone and the decrease in the detection limit of the aldehyde.

Hence, micellar media of the cationic surfactants favor the increase in solubility of the aci-forms of hydrazones and their stabilization. The above-mentioned effects can be used in the photometry of the lagre number of carbonyl compounds (ketones, aldehydes, and quinones) without using toxic solvents, extraction, and prolonged heating.

EXPERIMENTAL

The electron absorption spectra were registered on a SF-46 spectrophotometer. The IR spectra were obtained on a FSM 1201 Fourier spectrometer in hexachlorobutadiene (4000–1800, 1500–1300 cm^{-1} and in mineral oil (1300–400 cm^{-1}). The derivatograms were taken on an OD-103 derivatograph in air in the temperature range 0–1000°C at heating rate 10°C/min. pH values were measured on pH-121 and pH-673 devices. Starting 2,4-dinitrophenylhydrazine (pure, TU-6-09- 2394-72), the aldehydes (*p-, m*-nitro, *p*-chloro-, *p*-dimethylamino-, 2,4-disulfobenzaldehydes, and *p*-dimethylaminocynnamaldehyde) were crystallized from aqueous ethanol (melting points checked [16]). Benzaldehyde and *p*-methoxybenzaldehyde were distilled before use. Cetylpyridinium chloride monohydrate, $C_{21}H_{38}NCl \cdot H_2O$ (pure for analysis, TU-6-09-15-121-74), sodium dodecylsulfate, $C_{12}H_{25}OSO_3Na$ (pure, TU-6-09-07-1816-93, main substance content 82.4±1.3%0), and hydroxyethylated alkylphenol OP-10, $C_{14}H_{23}O(C_2H_4O)_{10}H$, (pure) were used as sur-

factants. The constant pH was maintained with the use of borate buffer solutions.

Synthesis of hydrazone from 2,4-dinitrophehylhydrazine and *p*-dimethylaminocynnamaldehyde. A weighed portion (0.0277 g) of 2,4-dinitrophenylhydrazine was dissolved in distilled water at heating in a 500 ml flask, and the solution obtained was acidified with concentrated HCl to pH 1. A weighted portion *p*-dimethylaminocynnamaldehyde (0.0492 g) was dissolved analogously. The hot solutions of reactant were mixed and heated at 80–90°C till complete coagulation of the precipitate obtained. The reaction mixture was thoroughly stirred and cooled. The precipitate was filtered off on a frit and washed with distilled water till the negative test for chloride ion with silver nitrate. The hydrazone obtained was dried at 110°C to remove the adsorbed moisture till the constant weight. The yield of the product was 70%. Found, %: C 57.46; H 4.82; N 19.71; O 18.01. $C_{17}H_{17}N_5O_4$. Calculated, %: C 57.88; H 4.47; N 20.05; O 17.60.

Evaluation of solubility of hydrazone in alkaline medium by isothermic saturation method. A weighed portion of the hydrazone synthesized, 0.05–0.1 g, was placed in a flask equipped with a glycerol seal and a stirrer, and 10 ml of the borate buffer (pH 13) was added to it. Cetylpyridinium chloride, 0.6 ml of 10^{-2} M solution, and 9.4 ml of the borate buffer was added to create the micellar medium. The rotation rate of the stirrer was chosen to provide the greater part of the solid phase to be in the suspended state. The establishing of the equilibrium in the heterogeneous system was checked by sampling once in an hour in the course of 6 h. The concentration of the hydrazone aci-form in water and water–micellar media was established using the corresponding calibration graphs. For evaluation of concentration of the hydrazone aci-form in the micelles of cetylpyridinium chloride the sample was preliminary diluted 10 times.

ACKNOWLEDGMENTS

The work was carried out with the financial support of the Federal Agency of Science and Innovations (grant no 2007-3-1.3-28-01-229).

REFERENCES

1. Brettle, R., *Obshchaya organicheskaya khimiya* (Comprehensive Organic Chemistry), Moscow: Khimiya, 1982, vol. 2, p. 488.
2. McMurry, J.E., *Chem. Communs*, 1968, no. 8, p. 443.
3. Kuznetsova, E.V., Tatarenko, S.A., Mil'kina, T.N., Morzhakova, T.M., Kudinova, L.M., and Batalin, O.A., *Neftekhimiya*, 1983, vol. 23, no. 5, p. 693.
4. Roper, K. and Zohn, H., *Leder*, 1992, vol. 43, no. 5, p. 117.
5. Vinuelas Cobo, J.L., Rodriguez Roldan, A., Botas Rabasa, M., and Garsia-Moreno del Rio, C., *A limentaria*, 1996, vol. 34, no. 269, p. 67.
6. Znerek, G., Lyftmann, H., and Karst, U., *Analyst*., 1999, vol. 124, no. 9, p. 1291.
7. Serikov, A.V., Berezkin, V.G., and Gogoman, I.V., *Zavod. Laborat.: Diagnost. Mater*., 2002, vol. 68, no. 9, p. 9.
8. Tang, J., Wang, X., Fen, Y., Sheng, G., and Fu, J., *Anal. Chem*., 2003, vol. 31, no. 12, p. 1468.
9. Fenaille, F., Tabet, J.-C., and Guy, P.A., *Anal. Chem*., 2004, vol. 76, no. 4, p. 867.
10. Sekine, Y., Oikava, D., Saiton, K., and Asano, Y., *J. Health Sci.*, 2005, vol. 51, no. 6, p. 629.
11. Saczk, A.A., Okumura, L.L., De Olivera, M.F., Zanoni, M.V.B., and Stradiotto, N.R., *Anal. and Bioanal. Chem*., 2005, vol. 381, no. 8, p. 1619.
12. Zhang, H-J., Huang, J.-F., Wang, H., and Feng, Y.-Q., *Anal. Chim. Acta*, 2006, vol. 565, no. 2, p. 129.
13. Korenman, I.M., *Fotometricheskii analiz. Metody opredeleniya organicheskikh soedinenii* (Photometric Analysis. Methods of Evaluation of Organic Compounds), Moscow: Khimiya, 1970.
14. Shinoda, K., Hakagava, T., Tamamusi, B., and Isemura, T., *Kolloidnye poverkhnostno-aktivnye veshchestva* (Colloid Surfactants), Moscow: Mir, 1966.
15. Gusakova, N.N., *Teoreticheskie i prikladnye aspekty primeneniya v fotometricheskom analize sistem pervichnye aromaticheskie aldegidy* (APAV Theoretical and Applied Aspects of Use of the Aromatic Aldehyde Anionic Surfactant Systems in Photometric Analysis), Saratov: SGAU, 2002.
16. Gordon, A. and Ford, P., *Sputnik khimika* (Chemist's Companion), Moscow: Mir, 1976.