# DIVINYL SULFIDE.

# COMMUNICATION 9. KINETICS AND MECHANISM OF REACTION OF PHENYLACETYLENE WITH SODIUM HYDROSULFIDE IN AQUEOUS DIMETHYL SULFOXIDE*

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A study of the kinetics of formation of cis,cis-di(2-phenylvinyl) sulfide (I) from $Na_2S$ and phenylacetylene hydrates in DMSO, hexamethylphosphoric triamide (HMPTA), and triethylphosphine oxide [2] showed that because of the limited solubility of $Na_2S$ in these solvents [3], it is difficult to vary the initial concentrations of the reagents, and hence also to establish the sequence of stages and order of reaction with respect to each of the reagents. We took into account the data in [4] on the specific extraction of NaSH from $Na_2S$ in DMSO, and in the present work we used a ready-made hydrosulfide. The latter compound is readily soluble in DMSO (∿10% at 20°C), so that the kinetics can be studied under homogeneous conditions. The aim of the present work was to study the kinetics of the reaction of phenylacetylene with NaSH in DMSO by various physicochemical methods, and the interpretation of its mechanism.

According to the data on the electrical conductivity of its solutions in DMSO, sodium hydrosulfide is practically completely dissociated into free ions. This is also indicated by a considerable shift in the PMR spectrum of a signal of the SH proton to a stronger field ($\delta$ − 3.5 ppm), with a reference to TMS), compared with the chemical shifts of protons of the SH group in thiols ($\delta$ 1.2-1.7 ppm). In accordance with these data, we then assumed that $C_{SH^-} = C_{NASH}$.

TABLE 1. Dependence of Initial Rate of Reaction of NaSH with Phenylacetylene (w) on Initial Concentrations of Reagents and Temperature

| T, °C | $w \cdot 10^4$, mole/liter·sec | Initial concentrations of reagents,* mole/liter | |
|---|---|---|---|
| | | PhC≡CH | NaSH |
| 60 | 1,49 | 0,78 | 1,40 |
| 80 | 6,08 | 0,79 | 1,40 |
| | 5,27 | 0,79 | 1,23 |
| | 2,20 | 0,79 | 0,59 |
| | 3,12 | 0,79 | 0,83 |
| | 2,68 | 0,58 | 0,83 |
| | 1,95 | 0,42 | 0,83 |
| | 4,73 | 1,07 | 0,83 |
| 100 | 16,8 | 0,86 | 0,89 |

*$C_{H_2O}$ = 3.08 mole/liter.

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*For communication 8, see [1].

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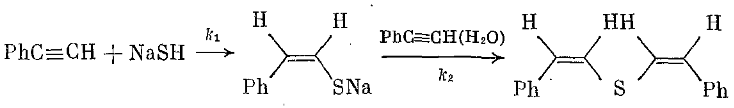
TABLE 2. Dependence of Rate Constants on Temperature and Values of Activation Parameters

| T., °C | Rate constants·$10^4$, liter/mole·sec | | Activation parameters | | | |
|---|---|---|---|---|---|---|
| | | | $\Delta H^{\neq}_{353}$, kJ/mole | | $\Delta S^{\neq}_{353}$, J/mole·deg | |
| | $k_1$ | $k_2$ | of $k_1$ | of $k_2$ | of $k_1$ | of $k_2$ |
| 60 | 1,47±0,05 | 4,9±0,1 | – | – | – | – |
| 80 | 5,47±0,15 | 23,1±0,5 | 76 | 87 | –107 | –67 |
| 100 | 21,9±0,5 | 110±4 | – | – | – | – |

Solutions of $Na_2S$ in DMSO are sky-blue in color [3, 4], which is explained by the formation of polysulfide ions $S_{2n}^{2-}$ or ion-radicals $S_n^{\cdot-}$ (n = 2-8) [5-7]. Solutions of NaSH in DMSO, obtained in an argon atmosphere, are colorless, but when air is passed through these solutions, the sky-blue color appears after a few seconds, and on storage in sealed ampuls, after about 24 h. If we compare the UV spectra of these colored solutions with the spectra of sodium polysulfides in DMSO and DMFA, a complete coincidence between the absorption band maxima is observed (λ 618, 505, and 435 nm) [5-7], and it can be concluded that the sky-blue color of the solutions of NaSH in DMSO is also related to the formation of polysulfide ions (or ion-radicals) as the result of oxidation of $HS^-$ or $S^{2-}$ ions (by oxygen from the air or DMSO). By using the known ε (2400) and λ (618 nm) [5], and also the Lambert–Beer law, we found that the maximal concentration of the polysulfide ions ($S_{2n}^{2-}$) is 0.5% of the NaSH concentration. Therefore, in the range of reagent concentrations studied, redox processes can be neglected, as confirmed by the results of kinetic studies described below, and the absence of side products. However, at low concentrations of water (<0.2 M), this factor must be taken into account.

The main results of the kinetic studies are given in Tables 1 and 2. As an example, in Fig. 1 we show the dependence of the concentration of reagents and reaction products on time at 60°C. The current concentrations are calculated directly from the PMR spectra (Fig. 2) according to the ratio between the integral intensities of signals of phenyl, vinyl, and acetylenic protons (5:2:1), whereby the concentration of the phenyl protons is retained in the course of the reaction. The consecutive-parallel reaction of formation of sulfide (I) proceeds with the formation of an intermediate cis-2-phenylvinylthiolate, and includes two second-order reactions (first-order with respect to phenylacetylene and the corresponding nucleophile, since the initial rate of consumption of NaSH is directly proportional to the initial concentration of phenylacetylene, and to that of NaSH)



(I)

The rate constant $k_1$ was calculated from the initial sections of the kinetic curves of NaSH consumption, while $k_2$ was found by solving a transcendental equation [8]

$$C_{PhCH=CHSNa(max)} = a_0 \cdot y^{y/(1-y)}$$

where $C_{PhCH=CHSNa(max)}$ is maximal concentration of intermediate thiolate; $a_0$ is initial concentration of NaSH; $y = k_2/k_1$.

The intermediate, cis-2-phenylvinylthiol could not be isolated as an individual compound, but the products of its reaction with ethyl and propyl bromides were identified. A solution containing a considerable excess of NaSH over PhC≡CH was heated until PhC≡CH was completely consumed (control by GLC), and the corresponding alkyl bromide was added. The products were identified by GLC at two phases, by comparison with actual samples of cis-PhCH=CHSEt and cis-PhCH=CHSPr. In the PMR spectra of the reaction mixtures, the appearance of the signal of the vinyl protons of sulfide (I) was preceded by a signal (δ 6.92 ppm) with an intensity proportional to the initial NaSH concentration, which corresponds to that calculated for cis-2-phenylvinylthiol. The signal disappears when excess of phenylacetylene is added, so that it

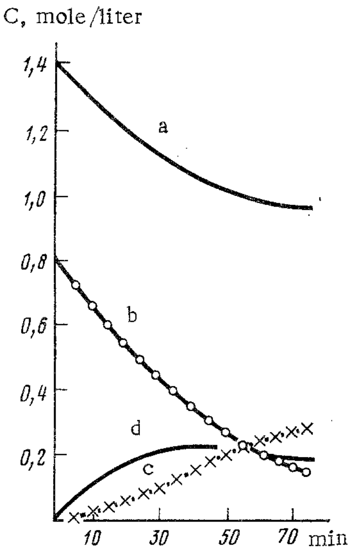


Fig. 1. Dependence of concentration of reagents and products in the reaction of PhC≡CH with NaSH in aqueous DMSO on time: a) NaSH; b) phenylacetylene; c) cis,cis-di(2-phenylvinyl) sulfide; d) cis-2-phenylvinylthiol. 60°C, $C_{H_2O}$ = 3.08 mole/liter.

can be assigned to vinyl protons of cis-2-phenylvinylthiol (or the corresponding thiolate). For the latter, based on data in [9], in the calculations dissociation into ions was considered to be complete.

All the experiments were carried out with a considerable excess of water in order not to introduce additional errors to the experimental data due to the influence of water on the reaction rate. The effect was estimated by the UV spectroscopic method. For this, every 10°C in the range of 50-100°C we determined the dependence of optical density D (λ319 nm) on time and the water concentration at 100°C. In the case, in contrast to the data obtained by PMR spectroscopy, it is impossible to carry out the calculations according to the initial sections of the kinetic curves, because of a background created by an intermediate product. For the kinetic curves, we calculated the transformation coefficients, from which the $E_{act}$ = 76 ± 1.9 kJ/mole was found, which agrees with the above data. For the more advanced stages of the transformation, $dC_{(PhCH=CH)_2S}/dt = k_1 \cdot C_{NaSH} \cdot C_{PhC\equiv CH}$ was taken, since the first stage of the reaction, being slower, is in fact the limiting one. According to our calculations, the error of such an assumption should not exceed 7% (taking into account the additivity rule $\varepsilon_{(PhCH=CH)_2S} \approx 2\varepsilon_{PhCH=CHSH}$ and the ratio $C_{PhCH=CHSH}/C_{NaSH} = [1 - (C_{NaSH}/a_0)^{(y-1)}](y-1)$ [8]). The dependence of $k_1$ on the water concentration in coordinates log $k_1$ vs. log $C_{H_2O}$ is linear, and log $k_1$ decreases with increase in log $C_{H_2O}$ (tangent of the slope angle = −1/3). The inhibiting influence of water is probably the result not of a protonation of the intermediately formed thiolate, since the acidity constant of thiols in DMSO is 10 orders of magnitude higher than that of water, but of hydration of a minimally solvated and very active SH anion [9]. According to the data in [10], in the DMSO–$H_2O$ mixtures, the cations are preferentially solvated by DMSO molecules, and anions by water molecules. Hence, the addition of $HS^-$ to acetylene includes an energy-consuming stage of anion dehydration, which should lead to a decrease in the reaction rate. A rectilinear dependence of $k_1$ on the water concentration is observed only in the range from 0.2 to 6 M. At lower concentrations, probably secondary polymerization and redox processes proceed (the appearance in UV spectrum of a shoulder with λ 345 nm and a large number of signals in the δ 5.5-7.4 ppm region in the PMR spectrum, and in addition, the reaction solution turns dark-brown). The high concentration of water strongly inhibits the reaction, although, in principle, an unsubstituted divinyl sulfide can be synthesized in water if a high pressure of acetylene is employed [4].

By reducing the data to $C_{H_2O}$ = 1 M at 100°C, we obtain a normalized expression for the initial rate of consumption of NaSH (w)

$$w = k_1^* \cdot C_{NaSH} \cdot C_{PhC\equiv CH} \cdot C_{H_2O}^{-1/3}$$

where $k_1^* = 1.51 \cdot 10^{-3}$ liter/mole·sec.

The above results can explain certain features of the reaction of acetylene with $Na_2S$ hydrates. Since the SH ion is active, $Na_2S$ may be a source of NaSH according to the scheme

$$Na_2S + H_2O \rightleftarrows NaOH + NaSH$$

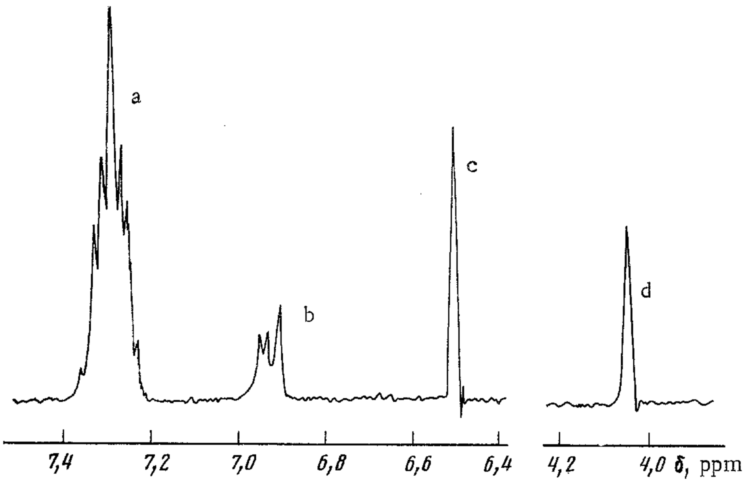


Fig. 2. PMR spectrum of the reaction mixture PhC≡CH + NaSH at 100°C. a) Ph; b) CH═CH of cis-2-phenylvinylthiol; c) CH═CH of cis,cis-di(2-phenylvinyl) sulfide; d) C≡CH.

The slight solubility of $Na_2S$ in DMSO ensures a fairly constant concentration of NaSH in the course of the reaction. The alkali, most of which does not dissolve in DMSO, plays the role of an aqueous buffer, regulating the concentration of water in the course of the reaction. Its positive influence on the yield of divinyl sulfide in the synthesis with $Na_2S \cdot 9H_2O$ at high acetylene pressures was shown in [4]. However, when the pressure of acetylene is decreased and $Na_2S \cdot 4H_2O$ is used, a negative influence of alkali is already observed, probably because of decrease in the solubility of acetylene and decrease in the concentration of NaSH in DMSO (a shift in equilibrium). There is an optimal ratio $Na_2S:H_2O$ = 1:4 [4]. At a lower water concentration, the reaction proceeds less well, because of decrease in the solubility of $Na_2S$, and at a high concentration, because of the inhibiting action of water, as shown above, and because of the side reaction in which 2,5-dimethyl-4-methylene-1,3-oxathiolane is formed [4].

In setting up a continuous process for the preparation of divinyl sulfide based on acetylene and $H_2S$, the use of NaSH as a reagent instead of $Na_2S$ does not introduce any substantial changes into the process flow diagram, but has definite advantages: homogenization of the reaction mixture, a higher rate of reaction, and less dependence on the concentration of water. It is interesting to note that a change in the water concentration of 30% when $Na_2S$ is used has a greater influence on the reaction rate than a 30-fold change in the case of NaSH.

## EXPERIMENTAL

In the determination of the electrical conductivity of the solutions we used an OK-102 conductometer. The measurements were carried out in a thermostated cell at 20 ± 0.1°C in an inert gas current. The apparatus was calibrated at 19°C with reference to KCl solution. The cell constant was 0.81. Preliminarily dried DMSO was distilled over $CaH_2$ at 50°C (2-3 mm) and stored over molecular 4-Å sieves. From the dependence of the electrical conductivity values (λ) of the NaSH solutions in absolute DMSO on $C_{NaSH}^{1/2}$, we graphically found the value of coefficient $\alpha^*$ in the Onsager equation $\lambda = \lambda_0 - \alpha^* \cdot C^{1/2}$ [11]. By the method of consecutive approximations, according to the Shedlovsky equation [12], we found the values of $\lambda_0$ and $K_D$

$$\frac{1}{\lambda \cdot S(F)} = \frac{1}{\lambda} + \frac{C \cdot \lambda \cdot S(F) \cdot f_{\pm}^2}{K_D \cdot \lambda_0^2}$$

where C is the concentration of NaSH in DMSO; $K_D$ is dissociation constant; $\lambda_0$ is electrical conductivity at infinite dilution; function $S(F) = [F/2 + \sqrt{1 + (F/2)^2}]^2$ and argument $F = \alpha^* \cdot \lambda_0^{-3/2} \cdot (C \cdot \lambda)^{1/2}$. The activity coefficients were calculated from the Debye–Hückel equation

[13], and the values of function S(F) were found from tables [14]. The values obtained were $\lambda_0 = 31.9\ \Omega^{-1}\cdot cm^2\cdot(g\text{-}eq)^{-1}$, $K_D = 0.89$ mole/liter. For example, for $C_{NaSH} = 0.01$ M, according to equation $K_D = C\cdot f_{\pm}^2\cdot\alpha/(1-\alpha)$, the value of the degree of dissociation obtained is $\alpha = 0.993$.

The PMR spectra were run on a Tesla BS-487C spectrometer (80 MHz) for DMSO solutions (internal standard DMSO). The chemical shifts were recalculated with reference to TMS (δ, ppm): 7.2-7.4 m ($C_6H_5$), 4.04 s (C≡CH), 6.92 m (cis-CH=CH) in 2-phenylvinylthiol, 6.49 and 6.53 two doublets with J = 11.8 Hz in sulfide (I). With increase in temperature, these doublets approach one another, and become degenerated into a singlet at 100°C (δ 6.51). This is probably due to a change in the contribution of the intermolecular components to the screening constant. To take the PMR spectra, the ampul with the sample solution was placed into a spectrometer sensor, preliminarily heated to the required temperature, and the spectra were recorded at given intervals of time. The concentration of phenylacetylene and sulfide (I) was calculated from the PMR spectra obtained; the concentration of NaSH and cis-2-phenylvinylthiol, from the material balance according to equation:

$$C^0_{\mathrm{NaSH}} = C_{\mathrm{NaSH}} + C_{\mathrm{PhCH=CHSH}} + C_{\mathrm{(PhCH=CH)_2S}}$$

$$C^0_{\mathrm{PhC\equiv CH}} = C_{\mathrm{PhC\equiv CH}} + C_{\mathrm{PhCH=CHSH}} + 2C_{\mathrm{(PhCH=CH)_2S}}$$

where $C^0$ are the initial concentrations of the reagents.

The UV spectra were run on a Specord UV-VIS apparatus. The solutions studied (0.062 M of NaSH and 0.286 M of PhC≡CH in DMSO) were sealed under Ar in 0.3 ml glass ampuls and thermostated (with an accuracy within ±0.1°C). At given intervals of time, the ampuls were in turn taken out and frozen to 0°C. The samples were then thawed, and diluted 10-fold with DMSO (error <1%). The spectra were run in quartz cuvettes ($l = 0.0057$ cm), using the analytical wavelength at λ 319 nm. By using the known value $\varepsilon = 2.94\cdot10^4$ for sulfide (I), we calculated its concentration and degree of transformation.

The GLC analysis was carried out on an LKhM-8MD chromatograph, with a katharometer as a detector, gas carrier He (30 ml/min), 2 m × 3 mm columns with 15% Carbowax and 5% silicone SE-30 on Chesasorb, and column temperature of 165°C.

## CONCLUSIONS

1. According to the data of kinetic study by UV and PMR spectroscopic methods, the formation of cis,cis-di(2-phenylvinyl) sulfide in the reaction between phenylacetylene and sodium hydrosulfide proceeds consecutive-parallel with the intermediate formation of cis-2-phenylvinylthiol, identified in the form of cis-2-phenylvinyl alkyl sulfides.

2. The rate constants at different temperatures and activation parameters of the consecutively-parallel reactions were estimated.

3. The formation of cis-2-phenylvinyl thiol is inhibited by water. At water concentrations in the range from 0.2 to 6 M, a rectilinear dependence is observed between the logarithms of the rate constants and the concentration of water.

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# RADIATION CHEMISTRY OF THE FLUOROOLEFINS

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The authors and their co-workers have shown that the fluoroolefins undergo extensive high-yield radical polymerization under β and γ irradiation. Low-yield radiolysis of the fluoroolefins also occurs here.

Radiational polymerization of the fluoroolefins is of interest since polymerization does not require the presence of chemical initiators in the system; initiation occurs at low temperatures; polymerization takes place in the solid monomer; and in certain cases, the monomer in question can be polymerized only with difficulty by other methods.

We have undertaken an extensive study of the radiation chemistry of the lower fluoroolefins with the aim of making known the possibilities of synthesizing fluorine-containing monomers and, at the same time, examining the chemical behavior of compounds of this type under irradiation. Study has been made of the radiolysis, homopolymerization, copolymerization, and graft copolymerization of the fluoroolefins.

Study has also been made of the macromolecules responsible for chain extension in the polymerization of tetrafluoroethylene (TFE). The kinetics of the radiational homopolymerization of TFE, trifluorochloroethylene, trifluoroethylene, vinyldiene fluoride, and vinyl fluoride have been investigated. The structures and properties of the resulting polymers have also been studied.

The results of these studies have been published in a series of articles [1-20]. The most detailed studies have been carried out on the heterogeneous radiational polymerization of TFE, in the gaseous and liquid phases and under the excess pressure of the monomer.

It was first shown that TFE is readily polymerized under β and γ irradiation. The radiochemical yield in the homopolymerization of TFE is one or two orders higher than the yields met in the homopolymerization of other unsaturated compounds, values as high as $I = 1 \cdot 10^6$ mole/100 eV being observed here.

TFE is readily polymerized, with extremely high radiochemical yield, under γ irradiation, so readily, in fact, that this monomer can be polymerized in the gaseous phase at atmospheric pressure and 20°C, or in the liquid phase at –78°C.

Hexafluoropropylene polymerizes much more slowly than TFE. A radiochemical yield of only 13 mole/100 eV is attained when this compound is irradiated at 20°C and a dose rate of 10 rad/sec. Complete polymerization (above 90%) of the monomer is attained only after irradiation for 300 h at a dose rate of 600 rad/sec. The product obtained from this type of reaction is a complex liquid oligomer with molecular weights in the 300-4000 range.

Irradiation to a dose of 250 Mrad at a dose rate of 600 rad/sec brought about no detectable change in perfluoroisobutylene.

Liquid-phase irradiation of trifluorochloroethylene at 20°C and a dose rate of 10 rad/sec led to the formation of a solid polymer, the radiochemical yield of the process being $5.5 \cdot 10^3$ mole/100 eV.

Studies on mass radiational polymerization were carried out with trifluorochloroethylene and trifluoroethylene. Radiational polymerizations of vinyldiene fluoride and vinyl fluoride

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