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STUDY OF THE REVERSIBLE REACTION BETWEEN THE DIPHENYLAMINYL RADICAL
AND STERICALLY HINDERED PHENOL

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UDC 541.124:542.91:541.515:547.551.2:547.56

Two methods of determining the equilibrium constant of the reaction of the diphenylaminyl radical with 2,4,6-tri-tert-butylphenol were proposed; they are based on the high reactivity of aminyl radicals in cleavage of a H atom from phenol and phenoxyl radicals in cleavage of an H atom from an amine. In the first method (generation of aminyl radicals in a system containing phenol and amine), the forward reaction goes into quasiequilibrium, and the maximum concentration of phenoxyl radical formed and the concentrations of the other components calculated from the stoichiometry are used for calculating the equilibrium constant. In the second method (kinetic features of consumption of the phenoxyl radical in the presence of amine and phenol), the reverse reaction goes into quasiequilibrium, and the equilibrium constant is calculated in this case using the initial segments of the kinetic curve of consumption of phenoxyl. Both methods give similar values of the equilibrium constant.

Reversible transfer of H between the diarylaminyl radical $Am^\cdot$ and shielded phenol PhOH plays an important role in explaining the catalytic effect of secondary aromatic amines AmH on the reaction of the sterically hindered phenoxyl radical $PhO^\cdot$ with hydroperoxide ROOH [1] and in interpreting the mechanism of the synergistic effect of mixed composites of AmH and PhOH [2]. However, due to experimental difficulties, the kinetics of this reaction have not been adequately studied for one pair of PhOH and $Am^\cdot$ [3, 4]. The purpose of the present study was to create a method for the quantitative estimation of the reverse reaction of $Am^\cdot$ with PhOH on the example of the diphenylaminyl radical $In^\cdot$ and 2,4,6-tri-tert-butylphenol ArOH.

EXPERIMENTAL

Thermal decomposition of tetraphenylhydrazine InIn in the presence of ArOH and diphenylamine InH and the kinetic features of consumption of the stable 2,4,6-tri-tert-butylphenoxyl radical $ArO^\cdot$ in the presence of InH and ArOH were investigated. The working temperature was 348 ± 0.2 K, CCl_4 was the solvent, and Ar was the atmosphere. The experiments were either conducted directly in the thermostated cuvettes of Spector UV-VIS (d 2.0 cm) and EPR RÉ-1306 spectrometers or in ampuls. In the latter case, the analysis of the reactive mixtures was
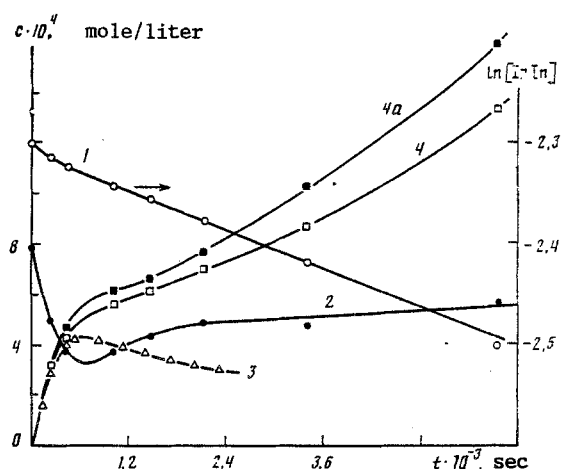
Fig. 1. Decomposition of InIn ($5 \cdot 10^{-3}$ mole/liter) in the presence of ArOH ($8 \cdot 10^{-4}$ mole/liter): 1) InIn, chromatographic analysis; 2) ArOH, IR analysis; 3) ArO·, EPR data (experiments in the spectrometer cell); 4) InH, chromatographic analysis; 4a) InH, IR analysis. CCl₄, 348 K, argon.

conducted by liquid chromatography on SiO_2 and IR spectrometry (Specord 75 IR, $d \leq 5$ cm) [5]. Since cooling to room temperature did not stop some processes which distort the results of the analyses, the spectra were periodically recorded for 30-40 min after the experiment, extrapolating the kinetic curves obtained in this way to the time of removal of the ampul from the thermostat (∿5 min) to decrease the error, and the depth of the extrapolation was 8-15%.

RESULTS AND DISCUSSION

The results of studying the decomposition of InIn in the presence of ArOH and InH are shown in Fig. 1. Extremes are clearly visible in the curves of consumption of ArOH and accumulation of ArO·. Addition of InH decreases the time for attaining the extremes t_{ext} and increases $[ArOH]_{ext}$ (in Fig. 1, $[ArOH]_{ext} \simeq 0.44 [ArOH]_0$, $t_{ext} \sim 10$-12 min). The rate constant of consumption of InIn k_d, maximum at the beginning of the experiment ($k_d = (1.4 \pm 0.1) \times 10^{-4}$ sec^{-1}), constantly decreases during the process to the unchanged value of $k_d = (0.7 \pm 0.07) \times 10^{-4}$ sec^{-1}. Although the first value of k_d reported coincides with constant k_1 of the rate of decomposition of InIn into radicals ($k_1 = 1.48 \cdot 10^{-4}$ sec^{-1} [6]), the second is characteristic of the decomposition of InIn in inert media in the absence of acceptance of In· [6]. In the initial stages, $v_{acc}^{InH} \approx v_{acc}^{ArO·} \approx v_{con}^{ArOH} \approx 2 v_{con}^{InIn}$. The equality $[ArOH]_0 = [ArO·] + [ArOH]$ was satisfied during the entire experiment.

The following sequence of reactions is the simplest explanation of the results obtained which does not contradict the data reported above

$$InIn \rightarrow In· + In· \tag{1}$$

$$In· + ArOH \rightarrow InH + ArO· \tag{2}$$

The rate constant k_d of decomposition of InIn, as noted in [7], has the maximum value of $k_d = k_1$. The rate of the reverse reaction increases as the products of reaction (2) accumulate

$$ArO· + InH \rightarrow ArOH + In· \tag{-2}$$

This results in an increase in [In·] and consequently an increase in the rate of reactions (−1) and a decrease in k_d. Since reaction (−1) is only one of the directions of self-recombination of In· [5, 8, 9], so that in the general case

$$In· + In· \rightarrow \text{Products} \quad (InIn, InH, \textit{o-, p-} \text{ semidines}) \tag{3}$$
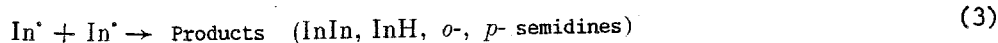
(the yield of InH attains ∿40%), we obtain an explanation for the appearance of the extremes (Fig. 1) in the kinetic curves of ArO· and ArOH [one of the products of the reverse reaction (2) can also be formed in the system according to independent reaction (3)]. It was experimentally established that in the presence of InH, the extremes on the curves of ArOH and ArO· become indistinct and the curves would turn into horizontal segments. This effect of InH
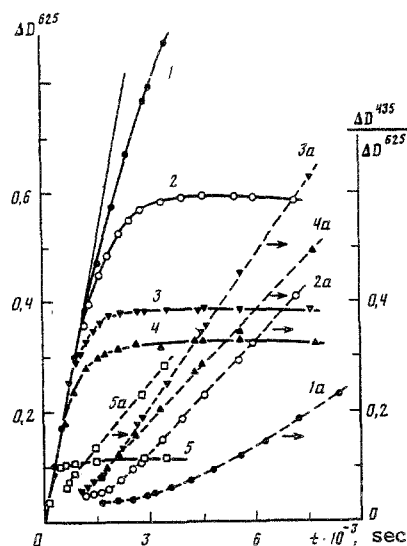
Fig. 2. Kinetic curves of the change in the optical density for λ 625 nm in experiments on decomposition of InIn ($1.5 \cdot 10^{-3}$ mole/liter) in the presence of ArOH and InH (C, mole/liter$\cdot 10^3$): 1) 5.6 and 0; 2) 1.6 and 0; 3) 0.8 and 0; 4) 1.6 and 1.6; 5) 1.6 and 8.0. Curves with the index a: change in the ratio $\Delta D^{435}/\Delta D^{625}$. Cuvette thickness of 2 cm.

becomes understandable if the changes in the concentration of the amine due to the occurrence of reaction (3) can be comparable to or even smaller than $[InH]_0$. The decrease in t_{ext} and the increase in $[ArOH]_{ext}$ when the experiments are conducted in the presence of InH can also be explained by the occurrence of reactions (−2) and (3). When $t = t_{ext}$, InH accumulates exclusively according to reaction (3), and there is already some amount of InH formed according to reaction (2) in the system. It was shown in [5] that the yield of InH in the initial stages of reaction (3) is strongly decreased by addition of InH, only increasing in the deeper stages. This apparently explains the character of the curve of accumulation of InH in Fig. 1, where the rate of formation of the amine is minimal near $t = t_{ext}$ and subsequently increases. The difference in the results of the IR and chromatographic analyses for InH (Fig. 1) is probably due to accumulation of semidines, which also have an N—H bond which absorbs at the analytical frequency of νNH 3420 cm^{-1} in the IR spectra.

It is not yet possible to construct a complete mathematical model of the process, since there are no data on the rate constants of the reactions of ArO$^\bullet$ and In$^\bullet$ with semidines and semidine radicals with ArOH, InH, and semidines of another degree of oligomerization. However, the data obtained permit determining the equilibrium constant K_2 within the framework of the explanation proposed above. It is necessary to consider the following.

1. Reactions (2) and (−2) begin to take place relatively rapidly in quasiequilibrium conditions. Actually, when consumption of InIn is neglected even in experiments without addition of InH, equality $\nu_2 \approx \nu_{-2}$ begins to be satisfied after time $t \approx (2k_1 k_{-2}[InIn]_0)^{-1/2}$. For the experiment in Fig. 1, for example, $t \sim 25$ sec, since $k_{-2} \sim 10^3$ liter/(mole·sec) [4].

2. During the experiment, $[In^\bullet]$ can only increase to a certain limit determined by the equality $\nu_1 = \nu_3$, i.e., after some time τ, the concentration of In$^\bullet$ attains the maximum value of $[In^\bullet]_\tau = (k_1[InIn]_\tau)^{1/2} k_3^{-1/2}$. It follows from the above that τ is almost equal to the time t_{ext} for attaining the extremes on the curves of ArOH and ArO$^\bullet$. Since reactions (2) and (−2) continue to take place in a quasiequilibrium mode at this time ($\nu_2 \approx \nu_{-2} \gg \nu_3$), then the value of K_2 can be calculated after determining the concentrations of the reactants.

Experiments were conducted directly in the cuvette of the spectrophotometer for determination of K_2, bypassing the stage of sampling and subsequent analysis (cf. Experimental). It was found that ArO$^\bullet$ [λ_{max} 625 nm, ε = 410 liter/(mole·cm)] is the sole colored compound only in the shallow stages (up to $t \lesssim t_{ext}$). A new, broader band with λ_{max} < 625 nm, which is shifted to the voilet region (under $\sim$580 nm) subsequently appears and increases in intensity;
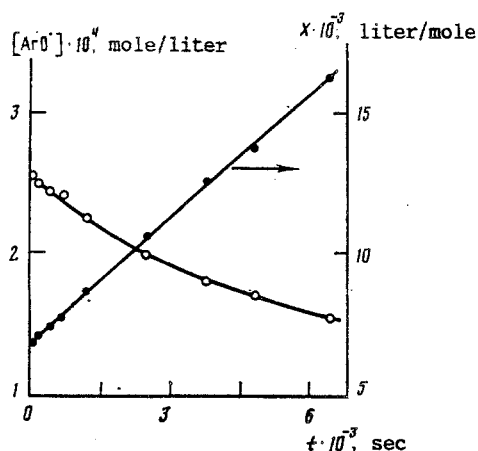
Fig. 3. Kinetic curve of consumption of $ArO^{\bullet}$ in the presence of ArOH ($2.7 \cdot 10^{-3}$ mole/liter) and InH ($1.5 \cdot 10^{-3}$ mole/liter) and its processing in the coordinates of Eq. (I), 348 K, CCl_4, argon.

the second, shorter-wave band of the new compound has λ_{max} on the boundary of the visible and UV regions. The indicated spectral complications make it difficult to choose the analytical wavelength for $ArO^{\bullet}$. Nevertheless, the presence of a slowly drifting isosbestic point on the long-wave wing of the absorption band of $ArO^{\bullet}$ at $\lambda \sim 625$ nm permitted using it as the analytical wavelength for small depths of the reaction up to the emergence of the curves of ΔD^{625} vs. t onto horizontal segments (Fig. 2); the same conclusion follows from the change in the ratio of $\Delta D^{435}/\Delta D^{625}$. The analysis of the curves of ΔD^{625} vs. t with consideration of the comments made shows that the curves of accumulation of $ArO^{\bullet}$ actually have a maximum positioned at the very beginning of the horizontal segments. This is in agreement with the data obtained with the ampul method. The initial segments of the curves in Fig. 2 permit finding the rate constant of generation of $In^{\bullet}$ in decomposition of InIn, $k_i = 2ek_1 = (2.7 \pm 0.1) \cdot 10^{-4}$ sec^{-1}. In comparing k_i with the value of k_1 reported above, we find the probability e of exit of radicals from the cage, e = 0.95. A similar value is obtained in comparing the rates of consumption of InIn with the rates of accumulation of InH and consumption of N-phenyl-2-naphthylamine in decomposition of InIn in the presence of this amine (cf. [6]).

Since the concentrations of the components are easily found from the stoichiometric relations: $[ArOH]_\tau = [ArOH]_0 - [ArO^{\bullet}]_\tau$; $[InH]_\tau = [InH]_0 + [ArO^{\bullet}]_\tau$; $[In^{\bullet}]_\tau = k_1[InIn]_\tau)^{1/2}k_3^{-1/2}$; $[InIn]_\tau = [InIn]_0 - 0.5 [ArO^{\bullet}]_\tau$; $K_2 = k_2/k_{-2} = [ArO^{\bullet}]_\tau[InH]_\tau/[In^{\bullet}]_\tau[ArOH]_\tau$ then K_2 can be determined from the curves of ΔD^{625} vs. t (Fig. 2). The value of $[ArO^{\bullet}]_\tau$ was found with ΔD^{625} on the horizontal segments, and time t was found with the time of emergence of the curves onto these segments. It was assumed that $k_3 = 1.8 \cdot 10^7$ liter/(mole·sec) [10]. K_2 was determined in two series of experiments with $[InIn]_0 = (0-8) \cdot 10^{-3}$ mole/liter; the results of some of the experiments are shown in Fig. 2. The values of K_2 found were almost independent of the conditions and had a probability of P = 0.95 $K_2 = (6.1 \pm 0.7) \cdot 10^3$ (CCl_4, 348 K).

The colored substance, which was different from $ArO^{\bullet}$, formed in the deep stages (for $t > t_{ext}$) is of special interest, since in explaining the events of catalysis of the reaction of $PhO^{\bullet}$ with ROOH under the effect of AmH [1] and the synergistic effect of mixtures of AmH with PhOH [2], it was assumed that $Am^{\bullet}$ and $PhO^{\bullet}$ radicals do not interact. The colored substance begins to form after a time which is slightly less than the time of emergence of the curves of ΔD^{625} vs. t into horizontal segments (Fig. 2). The induction period and rate of accumulation of substance in going out of the induction period are decreased by addition of InH, and addition of ArOH increases the induction period and virtually does not affect the rate; the rate of accumulation of the substance in the postinduction period also increases with an increase in the concentration InIn. If the dependences of the rate of accumulation of the substance (in optical density units/cm·sec at λ 435 nm, where $ArO^{\bullet}$ virtually does not absorb) on the product of $[ArO^{\bullet}]_\tau[In^{\bullet}]_\tau$ and $[ArO^{\bullet}]_\tau[In^{\bullet}]_\tau^2$ are plotted, lines which pass through the origin of coordinates (the dispersion for the first dependence is slightly less than for the second) can be obtained in both cases within the limits of the experimental precision. It is thus still impossible to determine whether the colored substance is a complex of $ArO^{\bullet}$ with $In^{\bullet}$ or $ArO^{\bullet}$ with the products of the reaction of $In^{\bullet} + In^{\bullet}$. Since elimination of $ArO^{\bullet}$ by

bubbling air through cooled solutions with the accumulated products results in consumption of the substance with the same rate as ArO·, the colored substance is apparently in equilibrium with ArO·.

The reverse reaction

$$In· + ArOH \underset{K_2}{\rightleftarrows} InH + ArO·$$
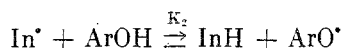
was also studied with the kinetic features of consumption of ArO· in the presence of InH and ArOH. The experiments were conducted directly in the cuvette of the spectrophotometer, recording the absorption spectra during the reaction. The spectral changes in this case differed from those described above. There are three isosbestic points at 367, 413, and ~500 nm (ε of 820, 130, and ~45 liter/(mole·cm), respectively) in the deep stages. The absorption band of ArO· at λ 625 nm can be used for analyzing ArO· without any corrections. A slight drift of all isosbestic points only begins when perceptible amounts of the products of recombination of In· have accumulated, and the picture increasingly begins to resemble the picture described for decomposition of InIn in the presence of ArOH. In analyzing the data on consumption of ArO·, it is necessary to consider the fact that addition of ArOH almost from the very beginning creates the conditions for the quasiequilibrium occurrence of reactions (−2) and (2), i.e., $v_2 \approx v_{-2} \gg v_3$ and $[In·] \approx K_2^{-1} [InH][ArO·]/[ArOH]$. The rate of consumption of ArO· is equal to the rate of quenching of In· radicals in the reaction with each other, i.e., $v_{con}^{ArO·} = 2k_3[In·]^2$. Integrating the last equation in consideration of the stoichiometric ratios and quasiequilibrium of reactions (−2) and (2), we obtain

$$\frac{c^2}{b^2} \frac{1}{[ArO·]} + 2\frac{bc + c^2}{b^3} \frac{|ArO·|}{b + [ArO·]} + \frac{(b + c)^2}{b^2} \frac{1}{b + [ArO·]} =$$
$$= 2k_3 K_2^{-2} t + const \qquad (I)$$
$$b = [InH]_0 - [ArO·]_0; \quad c = [ArOH]_0 + [ArO·]_0$$

or: $X = 2k_3 K_2^{-2} t + const$, where $const = X|_{t=0}$. Linearization of the curves of consumption of ArO· in the coordinates of Eq. (I) (Fig. 3) permit finding the value of parameter $2k_3 K_2^{-2} = 1.5 \pm 0.2$ liter/(mole·sec). Hence, in consideration of $k_3 = 1.8·10^7$ liter/(mole·sec) [10], we obtain $K_2 = (4.9 \pm 0.4)·10^3$ (CCl$_4$, 348 K). The result obtained satisfactorily coincides with the value reported above $(6.1 \pm 0.7)·10^3$, and the average value is $K_2 = (5.5 \pm 1)·10^3$.

We will use the value of K_2 found for several calculations. We will first estimate the strength of the N—H bond in the diphenylamine molecule. As previously in [4], assuming RT ln $K \approx -\Delta H_T^{\circ}$, we obtain $\Delta H_{348}^0 = -25$ kJ/mole. Since the strength of the O—H bond in ArOH is equal to 339.5 kJ/mole [11], then $D_{N-H} = 364.5$ kJ/mole, which is in agreement with the data in [12]. Secondly, we will find the rate constant of the reaction of In· with cumyl hydroperoxide ROOH at 348 K. We will use the results of the study of the catalytic activity of InH in the reaction of ArO· with ROOH, where we obtained $k_{In·+ROOH}/K_2 = 10^{6·9}$ exp (−38,200/RT) = 14.7 liter/(mole·sec) at 348 K. Assuming $K_2 = (5.5 \pm 1)·10^3$, we obtain $k_{In·+ROOH} = (8.1 \pm 1.6)·10^4$ liter/(mole·sec), which is in satisfactory agreement with the value of $1.1·10^5$ liter/(mole·sec) [12]. As we see, having the data for K_2 for different aminyl radicals and ArOH, it is possible to use the phenomenon of catalysis of the reaction of ArO· with ROOH under the effect of amines as a method for determining the absolute rate constants of cleavage of an H atom from ROOH with aminyl radicals.

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MILLIMETER SPECTROSCOPIC STUDY OF INTERMOLECULAR INTERACTIONS IN SOLUTIONS.

3.* EFFECTS OF HYDRATION IN AQUEOUS SOLUTIONS OF ALCOHOLS

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The absorption of 5 cm^{-1} electromagnetic radiation by aqueous solutions of methyl, ethyl, n-, and isopropyl, sec-, iso-, and tert-butyl, and tert-amyl alcohols and ethylene glycol was measured within their solubility limits in water at 20°C. It was found that the observed nonadditivity of absorption (absorption deficit) is a qualitative measure of hydration of alcohols of two types: hydrophilic and hydrophobic. The possibility of distinguishing these effects by millimeter spectroscopy was demonstrated. Hydrophobic hydration makes the basic contribution to the hydration number of aliphatic alcohols. On the example of solutions of ethanol and tert-butanol, it was shown that hydrophobic hydration decreases with an increase in the temperature of the solution due to intensification of hydrophobic interactions between the hydrocarbon radicals.

The state of the solvent in aqueous solutions of amphiphilic organic nonelectrolytes changes due to the formation of molecules of water by H bonds with polar groups (hydrophilic hydration) and reorganization of the system of H bonds between the molecules of water around nonpolar groups (hydrophobic hydration). The nonadditivity of the physical properties of the solutions observed in this case in principle permits studying water—nonelectrolyte intermolecular interactions (IMI).

We previously showed that absorption (α, dB·mm^{-1}) of extremely high frequency (EHF) electromagnetic radiation in the region of 10-2 cm^{-1} is very sensitive to both the composition of the solution and to the nature of the nonelectrolyte [1-3]. Significant nonadditivity of the EHF absorption α_{ef} was observed for strong IMI of the nonelectrolyte with water

$$\alpha_{ef} < \alpha_0 \equiv \varkappa_1 C_1 + \varkappa_2 C_2 \qquad (1)$$

where C_i and $\varkappa_i$ are the molar concentrations and extinction coefficient, respectively, and i = 1 (water) and 2 (nonelectrolyte).

In dilute solutions, water makes the basic contribution to the absorption ($C_1 > C_2$, $\varkappa_1 > \varkappa_2$). The high absorption capacity of water in the EHF region is due to the presence of a fraction of freely rotating molecules [3] which form no more than one H bond with the environment. In binding of a water molecule by the molecule of the nonelectrolyte no less stably than in the bulk of the solvent, all of its rotational degrees of freedom are frozen with relaxation times of $\tau > 10$ psec. If the entire absorption deficit $\delta\alpha = \alpha_0 - \alpha_{ef}$ is attributed to immobilization of the water molecules in the hydrate shell, then it will be possible to estimate the hydration number N, i.e., the average number of water molecules with frozen rotational degrees of freedom under the effect of the molecule of the dissolved substance on conversion to one molecule of the nonelectrolyte

$$N = N_\gamma = \delta\alpha / \varkappa_1 C_2 \qquad (2)$$

However, the hypothesis that both the hydration water and the hydrated nonelectrolyte stop interacting with the EHF radiation as a result of the IMI is more realistic

$$N = N_\theta = (\delta\alpha - \varkappa_2 C_2)/\varkappa_1 C_2 \qquad (3)$$

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*For previous communication, see [1].