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Initial State and Transition State Solvation in Oxidative Dimerization of Styrene in the Presence of Palladium(II) Acetate in Various Solvents

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Kinetics of oxidative dimerization of styrene to give E,E-1,4-diphenyl-1,3-butadiene in the presence of palladium(II) acetate has been studied in 12 solvents. In all solvents studied, the reaction obeyed the second order kinetics. Activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$) were evaluated and isokinetic relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ was established. The trimeric structure of palladium(II) acetate has been supported by spectrophotometric measurements in all solvents except acetonitrile. From the solubility data of palladium(II) acetate its Gibbs free energies of transfer ($\delta\mu^{o}_{Pd}$) from heptane (reference solvent) to the respective solvent were calculated. The same values for styrene ($\delta\mu^{o}_{St}$) were obtained from the partition constants of styrene between solvents studied and the phase of cross-linked polymer. From $\delta\mu^{o}_{Pd}$, $\delta\mu^{o}_{St}$, and $\delta\Delta G^{\neq}$ values transfer functions of transition state $\delta\mu^{\neq}$ were calculated. Correlations of transfer functions of the initial state and the transition state with empirical solvent parameters were examined and used in discussion of a reaction mechanism.

Introduction

Recently a quantitative approach to interpretation of solvent effects on reaction kinetics was developed on the basis of different types of correlation equations [1–7]. In this paper this approach is applied to the reaction of oxidative dimerization of styrene in the presence of Pd(II) acetate:

$$2\ PhCH{=}CH_2 + Pd(OAc)_2 \rightarrow$$

$$PhCH{=}CH{-}CH{=}CHPh + Pd(O) + 2HOAc \qquad (1)$$

whose kinetics and mechanism have been studied earlier in the acetate medium [8]. It turned out that reaction (1) proceeds with easily measurable rates in many solvents and this makes it a convenient object for application of the correlation approach.

While studying solvent effects on kinetics of chemical reactions it is of substantial importance to separate effects of the initial state and the transition state solvation [6, 9]. This implies an independent determination of reagents ($\delta\mu^{o}_{R}$) free energies of transfer from some reference solvent to other solvents, which are used in kinetic experiments. However, for such substances as styrene, possessing an extremely good solubility in most organic solvents and too low volatility, all known methods of $\delta\mu^{o}_{R}$ determination [9] can be hardly used. That is why the new method of $\delta\mu^{o}_{R}$ estimation, applicable, in principle, to all substances and based on utilization of 'solid phase co-solvent', is presented in this paper [10].

Results and Discussion

I. The State of Pd(II) Acetate in Organic Solvents

Depending on temperature, concentration, and the presence of alkaline metal acetates, various forms of Pd(II) acetate can exist in solution and it is known [12, 13], that transformations of one form to another are accompanied by considerable changes in visible and near ultraviolet spectral regions. So one can control the Pd(II) acetate form in all solvents by observing its absorption spectra.

Table I collects spectral characteristics of Pd(II) acetate in solvents used. For all solvents except DMSO and DMF only one absorption band was observed. It is seen that for 8 solvents: dioxane, benzene, ethyl acetate, acetone, carbon tetrachloride, chloroform, acetic acid, and acetic anhydride the wavelength of maximum absorption, λ_{max}, and the extinction coefficient, ϵ_{max}, remain almost constant. For two solvents from the above group (benzene and acetic acid) the trimeric structure, $Pd_3(OAc)_6$, of Pd(II) acetate was established at room temperature [11]. This supports the assumption that in the remaining 6 solvents the form $Pd_3(OAc)_6$ is dominant.

TABLE I. Wavelengths of Maximum Absorption (λ_{max}) and Molar Extinction Coefficients (ϵ) for Pd(II) Acetate in Organic Solvents at 25 ± 2 °C.

Solvent	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
Dioxane	396	201
Benzene	395	216
Ethyl acetate	396	207
Acetone	396	208
Carbon tetrachloride	396	170
Chloroform	395	205
Acetic acid	395	177
Acetic anhydride	394	188
N,N-Dimethylformamide	377[a]	258
Dimethyl sulphoxide	350[a]	720
Acetonitrile	325–340[b]	237[c]

[a] Maximum position obtained after separation of spectra to components according to [14]. [b] The position of the absorption band shifts to shorter wavelength on dilution. [c] At 330 nm.

In DMSO and DMF there is a strong increase in absorption in the ultraviolet region and the band near 400 nm remains only as a shoulder. Separation of spectra to components according to [14] gives the values λ_{max} and ϵ_{max} included in Table I. It is seen that in these solvents the maximum position and the intensity of the band is markedly changed indicating the strong solvation of Pd(II). Depolymerization of trimer, apparently, does not occur since the Beers law is carried out satisfactorily in the both solvents in a wide concentration range of Pd(II).

The most pronounced spectral changes are observed in acetonitrile solvent (Table I). The blue shift of the Pd(II) peak on dilution shows an appreciable depolymerization of trimer in this solvent.

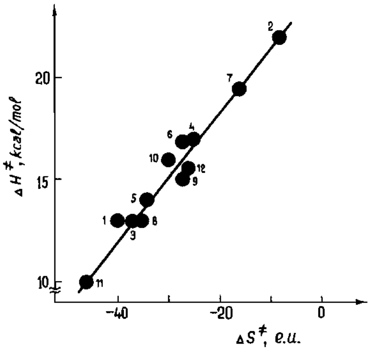

Fig. 1. Isokinetic relationship for reaction (1) according to data from Table II.

II. Kinetics of Oxidative Dimerization of Styrene

The rate of reaction (1) in all solvents included in Table I in a temperature range of 20–55 °C follows the simple kinetics of the type:

rate = k[Pd(II)] [styrene]

Rate constants k and evaluated from their temperature dependencies activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ together with $\Delta G^{\neq}$ values are summarized in Table II. Besides these solvents triethylamine, hexamethylphosphorictriamide, and methanol were also tested. In the first two solvents Pd(II) acetate did not react with styrene even at elevated temperatures (80 °C), presumably, due to formation of stable, low reactive solvates of the $Pd(OAc)_2(Solv)_2$ type [11] in these highly donor solvents. In methanol, addition of styrene caused rapid Pd(II) reduction to Pd(0). However, the product of reaction (1), E,E-1,4-diphenyl-1,3-butadiene, was not formed. In this solvent the reaction, probably, proceeds according to another pathway to give the respective acetals and ketals [15].

TABLE II. Rate Constants and Activation Parameters of Reaction (1) in Various Solvents at 25 °C.

No.	Solvent	$10^6 \times k/M^{-1}$ s^{-1}	$\Delta H^{\neq}$/kcal/mol	$\Delta S^{\neq}$/e.u.	$\Delta G^{\neq}$/kcal/mol
1	Dimethyl sulphoxide	0.90 ± 0.05	12.6 ± 0.9	−40 ± 5	25.60
2	n-Heptane	1.2 ± 0.1	22 ± 2	−8 ± 7	25.50
3	Ethyl acetate	1.3 ± 0.03	13 ± 1	−37 ± 3	25.40
4	Dioxane	1.6 ± 0.1	17 ± 2	−25 ± 6	25.30
5	N,N-Dimethylformamide	2.5 ± 0.1	14 ± 2	−34 ± 6	25.00
6	Benzene	2.8 ± 0.2	16.9 ± 0.8	−27 ± 3	24.95
7	Acetone	4.0 ± 0.1	19.5 ± 0.7	−16 ± 2	24.75
8	Acetonitrile	4.7 ± 0.3	13 ± 1	−35 ± 5	24.65
9	Carbon tetrachloride	6.0 ± 0.4	15 ± 2	−27 ± 6	24.50
10	Chloroform	7.3 ± 0.8	16 ± 2	−30 ± 7	24.40
11	Acetic anhydride	19 ± 1	10 ± 5	−46 ± 17	23.80
12	Acetic acid	59 ± 4	15.5 ± 0.5	−26 ± 2	23.10

TABLE III. Transfer Functions and Empirical Solvent Parameters[a] at 25 °C.

No.	Solvent	$\delta\mu^{o}_{Pd}$ (kcal/mol)	$\delta\mu^{o}_{St}$ (kcal/mol)	$\delta\Delta G^{\neq}$ (kcal/mol)	$\delta\mu^{\neq}$ (kcal/mol)	$(\epsilon - 1)/(2\epsilon + 1)$	E_T (kcal/mol)	DN (kcal/mol)	AN	π^*
1	Dimethyl sulphoxide	−4.42	−0.08	0.10	−4.40	0.485	45.0	29.8	19.3	1.000
2	n-Heptane	0	0	0	0	0.190	30.9[b]	0[e]	0[b]	−0.081
3	Ethyl acetate	−3.17	0.16	−0.10	−3.10	0.384	38.1[c]	17.1	–	0.534
4	Dioxane	−3.89	−0.13	−0.20	−4.20	0.223	36.0	14.8	10.8	0.553
5	N,N-Dimethylformamide	−4.29	−0.65	−0.50	−4.45	0.480	43.8	26.6	16.0	0.875
6	Benzene	−2.88	0.003	−0.55	−3.40	0.230	34.5	0.1	8.2	0.588
7	Acetone	−3.58	0.16	−0.75	−4.17	0.465	42.2	17.0	12.5	0.683
8	Acetonitrile	−3.31	0.22	−0.85	−3.95	0.480	46.0	14.1	18.9	0.713
9	Carbon tetrachloride	−1.09	0.47	−1.0	−1.60	0.225	32.5	0[e]	8.6	0.294
10	Chloroform	−4.61	−0.12	−1.1	−5.85	0.356	39.1	0[e]	23.1	0.760
11	Acetic anhydride	−2.79	0.34	−1.7	−4.15	0.465	43.9[d]	10.5	–	0.742
12	Acetic acid	−2.44	0.27	−2.4	−4.55	0.388	51.2	9.6[f]	52.9	0.664

[a] Values E_T, DN, and AN are taken from [4, 5], π^* from [22]. [b] Values for n-hexane. [c] Taken from [19]. [d] Taken from [24]. [e] Values assumed to be close to zero. [f] Obtained from eqn. B = 47 + 9.6 DN, where B is Koppel-Palm parameter [1].

It is seen from Table II that $\Delta H^{\neq}$ and $\Delta S^{\neq}$ vary markedly throughout the solvent series; $\Delta H^{\neq}$ lowering is compensated by $\Delta S^{\neq}$ decrease. Relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is shown in Fig. 1*, from which it is clear that the linear dependence exists between these two parameters. According to several authors [16, 17] existence of such isokinetic relationship can be indicative of a common mechanism in a whole series. This result, together with the spectral data from Section I, gives evidence that the rate constant k in all solvents, possibly except acetonitrile, characterizes the process with a common mechanism and with common reactive species.

According to the previous results [8] the rate determining step of reaction (1) involves the bimolecular interaction of Pd(II) acetate with styrene, possibly through the intermediate π-complex formation, to give styrylpalladium derivative:

$$Pd_3(OAc)_6 + PhCH{=}CH_2 \rightarrow$$

$$Pd_3(OAc)_5{-}CH{=}CHPh + HOAc \qquad (2)$$

The subsequent fast reductive decomposition of the latter gives final reaction products. The mechanism of step (2) as it was suggested by Henry can be represented by analogy with aromatic electrophilic substitution [15]:

$$Pd_3(OAc)_6 + PhCH{=}CH_2 \rightleftharpoons$$

$$Pd_3(O\bar{A}c)_6{-}CH_2{-}\overset{+}{C}HPh\ (I) \rightarrow$$

$$Pd_3(OAc)_5{-}CH{=}CHPh + HOAc$$

Conversion of σ-complex I to styrylpalladium derivative implies the proton transfer from methylene carbon. This proton transfer step appears to be significant in overall kinetics since the noticeable deuterium kinetic isotope effect $k_{PhCH=CH_2}/k_{PhCH=CD_2} = 3$ was found in reaction (1) [18]. The proton transfer is, probably, assisted by the acetate ion, since the presence of acetate ions is necessary to promote oxidative dimerization of olefins [8, 15]. A probable transition state of step (2) must thus involve σ-complex I, in which methylene C–H bond of styrene fragment is weakened due to interaction with acetate. This should lead to the lowering of charges in I; the limiting situation being possible in which the complete synchronization of Pd–C bond formation and C–H bond cleavage can be achieved. In this case no charge separation will occur in the transition state. The useful information about a degree of the charge separation in the transition

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*The solvents in all figures may be identified from their numbers by reference to Tables II–IV.

TABLE IV. Solubilities of Pd(II) Acetate (S_{Pd}) and Partition Constants of Styrene (P_{St}) between the Polymer Phase (Polysorb-1) and Organic Solvents at 25 °C.

No.	Solvent	S_{Pd}[a], M	P_{St}[b], cm^3/g
1	Dimethyl sulphoxide	0.91	1.4
2	n-Heptane	0.00052	1.6
3	Ethyl acetate	0.11	1.2
4	Dioxane	0.37	1.3
5	N,N-Dimethylformamide	0.73	0.53
6	Benzene	0.067	1.7
7	Acetone	0.22	2.1
8	Acetonitrile	0.14	2.4
9	Carbon tetrachloride	0.0033	3.5
10	Chloroform	1.25	1.3
11	Acetic anhydride	0.058	0.9
12	Acetic acid	0.032	2.5

[a] Relative standard deviation does not exceed ±3%. [b] Relative standard deviation does not exceed ±30%.

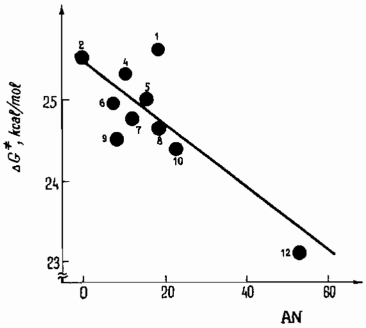


Fig. 2. Correlation between $\Delta G^{\neq}$ for reaction (1), Table II, and solvent acceptor numbers AN.

state can be obtained from the study of solvent effect on the reaction rate.

III. Initial State Solvation

Palladium(II) Acetate

From the solubility data of Pd(II) acetate collected in Table IV (see Experimental) one can calculate [9] the change in the standard chemical potential or Gibbs free energy of transfer (throughout the paper standard state is 1.0 *M*):

$$\delta\mu^{\circ}_{Pd} = RT \ln(S^{\circ}_{Pd}/S_{Pd}) \tag{3}$$

where S_{Pd} and S°_{Pd} are solubilities of Pd(II) acetate in an arbitrary solvent and in a reference solvent respectively. Values $\delta\mu^{\circ}_{Pd}$ calculated using n-heptane as a reference solvent are collected in Table III.

Styrene

In this case solubility data cannot be used since styrene mixes infinitely with most solvents studied. Other methods include evaluation of $\delta\mu^{\circ}_{R}$ either from Henry constants for high volatile substances or from partition constants of a given substance between the solvents under study and some additional solvent which is immiscible with all of them. In our case both these approaches are inapplicable and we have tried to improve the latter using the phase of cross-linked polymer as an additional co-solvent. Its insolubility provides the necessary immiscibility with any solvent and a sole source of unaccuracy of the method comes from a swelling of the polymer phase. The closed values of partition constants were however obtained for two samples of polymer having different linkage degree and thus swelling as it is shown in Experimental. From the data in Table IV one can calculate the change in the standard potential according to:

$$\delta\mu^{\circ}_{St} = RT \ln(P_{St}/P^{\circ}_{St})$$

where P_{St} is the partition constant of styrene between the polymer phase and an arbitrary solvent and P°_{St} is the same value for a reference solvent. Values $\delta\mu^{\circ}_{St}$ calculated using n-heptane as a reference solvent are collected in Table III.

IV. Transition State Solvation

The change in the chemical potential of the transition state, $\delta\mu^{\neq}$, may be calculated according to [6]:

$$\delta\mu^{\neq} = \delta\mu^{\circ}_{Pd} + \delta\mu^{\circ}_{St} + \delta\Delta G^{\neq} \tag{5}$$

Values $\delta\mu^{\neq}$ (n-heptane as a reference solvent), obtained from data in Tables II and III, are collected in Table III.

V. Solvent Effects on Kinetics of Oxidative Dimerization

Correlation of $\Delta G^{\neq}$

Table III gives the most widely used empirical solvent parameters such as Kirkwood function $(\epsilon - 1)/(2\epsilon + 1)$, Dimroth-Reinhardt E_T parameters [19], Gutmann donor numbers DN [20], acceptor numbers AN [21], Kamlet and Taft π^* parameters [22]. Establishment of linear correlations between the free energies of transfer of various reactants or transition states and any of these parameters is indicative of the contribution of a definite type of interaction to the solvation energies of these species. We shall first consider the correlation of $\Delta G^{\neq}$ which can be obtained directly from the rate constants.

Analysis of data in Table III shows that $\Delta G^{\neq}$ does not correlate satisfactory with most of parameters. Correlation coefficients (r) for dependencies of $\Delta G^{\neq}$ on $(\epsilon - 1)/(2\epsilon + 1)$, E_T, DN, and π^* are

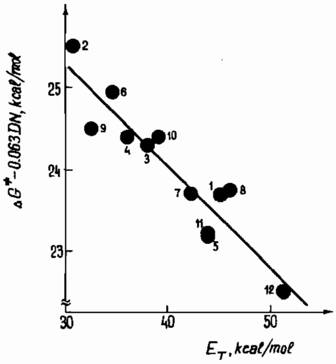


Fig. 3. Graphical representation of two-parameter equation (7).

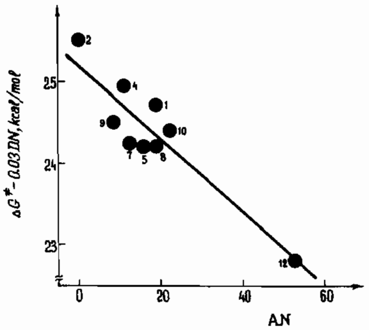


Fig. 4. Graphical representation of two-parameter equation (8).

equal to 0.21, 0.54, 0.30, and 0.18 respectively with the boundary value r = 0.58, when number of degrees of freedom f = m − 2 = 10 and probability P = 0.95. Only in the case of AN r = 0.82 with the boundary value r = 0.63 and f = 8 (for ethyl acetate and acetonitrile AN values are unknown). The plot $\Delta G^{\neq}$ *versus* AN is presented in Fig. 2. It is seen, however, that correlation is rather poor indicating well pronounced contributions of interaction of other types. In general, AN values correlate with E_T; there is no, however, good linear regression [21]. So the existence of correlation between $\Delta G^{\neq}$ and AN and the absence of it between $\Delta G^{\neq}$ and E_T, possibly comes from an occasional choice of these particular solvents. On the whole it is noteworthy that single parameter correlations are unsatisfactory in this case.

The failure to establish simple single-parameter correlations necessitates a simultaneous consideration of several properties of solvents which are characeterised by different parameters. The simplest way to do this is to introduce two-parameter correlations of the type:

$$\Delta G^{\neq} = A_0 + A_1X + A_2Y \qquad (6)$$

where A_0, A_1, and A_2 are constants, and X and Y are solvent parameters. This approach has been successfully applied to describe solvent effects on kinetics of nucleophilic substitution reactions. Different pairs of parameters have been used, namely, E_T and DN [24, 25], AN and DN [26], and some others [27]. Evidently the choice of the proper pair should be based on statistical criterion considering X and Y as independent variables. The same criterion was used above in the case of single-parameter correlations. Correlation coefficients were calculated for all possible pairs of parameters from Table III and the best correlations turned out to be observed for pairs E_T and DN in the form:

$$\Delta G^{\neq} = 29.1 - 0.125\,E_T + 0.063\,DN \qquad (7)$$

with r = 0.93 and AN and DN in the form:

$$\Delta G^{\neq} = 25.2 - 0.045\,AN + 0.030\,DN \qquad (8)$$

with r = 0.92. Graphical illustrations to eqns. (7) and (8) are given in Figs. 3 and 4. As it was noted above, AN correlates with E_T, so eqns. (7) and (8) as a matter of fact are similar.

The rate retardation by donor solvents (growth in $\Delta G^{\neq}$ with increase in DN) can be a result of stabilization of the initial state, if desolvation of $Pd_3(OAc)_6$ is necessary for interaction with styrene, or destabilization of the transition state, if solvation of $Pd_3(OAc)_6$ is retained and more donor solvents while coordinating with Pd(II) weaken its bond with styrene. The same uncertainty remains for E_T (or AN) contribution to the reaction rate; however, destabilization of the initial state by polar solvents at first sight seems to be less probable, than stabilization of the transition state. The next Section is devoted to separation of the effects of initial and transition states.

Correlation of $\delta\mu^{\circ}_{Pd}$ and $\delta\mu^{\neq}_{R}$. Separation of Initial State and Transition State Effects

To begin with, the attention must be paid to relative contributions of $\delta\mu^{\circ}_{Pd}$, $\delta\mu^{\circ}_{St}$, and $\delta\Delta G^{\neq}$ to a resulting $\delta\mu^{\neq}$ value. Although the rate difference in extreme cases (DMSO and HOAc) reaches almost two orders of magnitude, $\delta\Delta G^{\neq}$ indexes for most solvents (No. 1–10 from Table III) vary in a range of ~1 kcal/mol, Table III. Also a small variation is observed for $\delta\mu^{\circ}_{St}$ values. In the same solvents, $\delta\mu^{\circ}_{Pd}$ values vary in a much wider range reaching 4.6 kcal/mol. So, the variation of $\delta\mu^{\neq}$ indexes appear to be in line with those of $\delta\mu^{\circ}_{Pd}$ and this situation is depicted in Fig. 5.

Weak dependence of $\delta\mu^{\circ}_{St}$ on solvent seems to be rather expected, since, as it was noted in [9], organic solvents poorly solvate unpolar substances. On the contrary, Pd(II) acetate, possessing metallic centers which can coordinate solvent molecules, is solvated

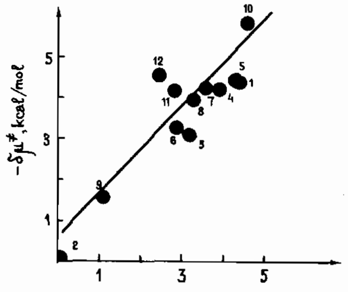


Fig. 5. Correlation between transfer functions of the transition state ($\delta\mu^{\neq}$) and Pd(II) acetate ($\delta\mu^{o}_{Pd}$).

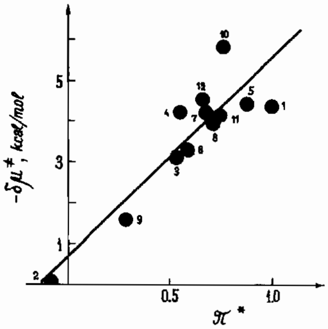


Fig. 8. Correlation between transfer functions of the transition state ($\delta\mu^{\neq}$) and Kamlet-Taft parameters π^*.

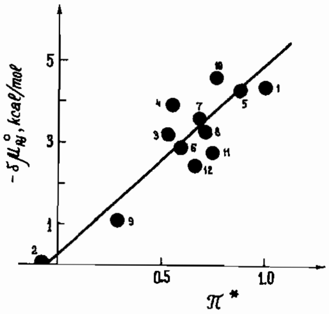


Fig. 6. Correlation between transfer functions of Pd(II) acetate ($\delta\mu^{o}_{Pd}$) and Kamlet-Taft parameters π^*.

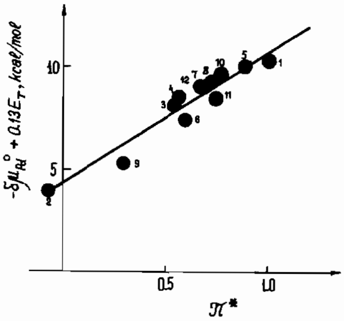


Fig. 7. Graphical representation of two-parameter equation (9).

stronger and $\delta\mu^{o}_{Pd}$ values appear to be more sensitive to the nature of the solvent. The dependence in Fig. 5 shows that this solvation remains in the transition state also. However, the very dependence of the reaction rate is indicative of a nonequivalent solvation of the initial state and the transition state. This implies the necessity of an independent consideration of the both states.

The dependence of $\delta\mu^{o}_{St}$ on solvent can be excluded from the consideration since, on one hand, it is weak and, on the other hand, unsystematic. We have failed to observe any correlation between $\delta\mu^{o}_{St}$ indexes and any solvent parameter as well as any their linear combination.

We found that $\delta\mu^{o}_{Pd}$ values were linear only with π^*, Fig. 6, according to:

$$\delta\mu^{o}_{Pd} = -4.34\,\pi^* - 0.39$$

with the correlation coefficient r = 0.89. When two-parameter approach was applied, the best correlation gave a combination of π^* with E_T, Fig. 7, in the following form:

$$\delta\mu^{o}_{Pd} = -6.42\pi^* + 0.13\,E_T - 4.35 \qquad (9)$$

with r = 0.96. It comes from eqn. (9), that $Pd_3(OAc)_6$ is better solvated with more polar solvents (negative coefficient at π^*). This inference seems sound considering the polar nature of $Pd_3(OAc)_6$ molecule. Destabilization of $Pd_3(OAc)_6$ by solvents with high E_T indexes is, however, not quite clear. Parameters E_T and π^* have much in common and correlate satisfactorily within the families of related solvents [22]. Their most pronounced difference lies, apparently, in the fact that E_T values contain an additional contribution resulting from the formation of hydrogen bonds and characterize an ability to solvate donor centers rather, than the solvent 'polarity' [5, 21, 22]. However, if $Pd_3(OAc)_6$ species contains such centers, their solvation should decrease $\delta\mu^{o}_{Pd}$ (negative coefficient at E_T); if not, no E_T contribution to $\delta\mu^{o}_{Pd}$ should be observed. We suppose that the positive contribution of E_T to $\delta\mu^{o}_{Pd}$ can be explained, for instance, in terms of a rupture of solvent intermolecular hydrogen bonds by large $Pd_3(OAc)_6$ molecules (mol. weight 672). It seems reasonable that ability to form such hydrogen bonds can correlate with E_T, since E_T values are directly proportional to δ^2 Hildebrand-Scatchard parameters, which reflect solvents internal cohesion [28].

It is expected from Figs. 5 and 6, that $\delta\mu^{\neq}$ values correlate with π^*, Fig. 8, according to:

$$\delta\mu^{\neq} = -4.86\pi^* - 0.68$$

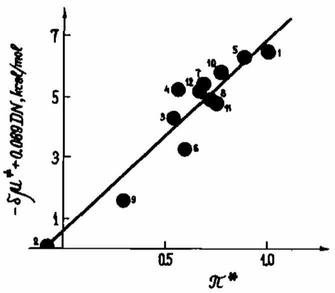


Fig. 9. Graphical representation of two-parameter equation (10).

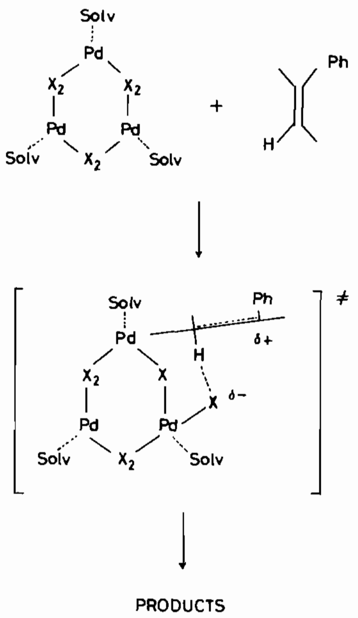
with r = 0.89. No correlation was observed with other parameters. In contrast to $\delta\mu^{\circ}_{Pd}$, however, addition of E_T as a second parameter does not appreciably improve this correlation (r = 0.91). Addition of DN gives a much better correlation:

$$\delta\mu^{\neq} = -6.52\pi^* + 0.069\ \mathrm{DN} - 0.47 \qquad (10)$$

with r = 0.95. Graphical illustration to eqn. (10) is presented in Fig. 9. It is seen from eqn. (10) that an increase in the solvent polarity (π^*) stabilizes the transition state to the same extent as it is observed for the initial state, eqn. (9). A positive contribution from DN, *e.g.* destabilization of the transition state by donor solvents, is in agreement with the assumption that solvation of palladium centers retains in the transition state, the latter weakening the palladium-olefin interaction. The weakening of the transition metal carbon bonds by coordination with donor molecules is well documented [29]. The absence of E_T contribution can be explained assuming that a donor center arises in the transition state, and its solvation compensates an unfavourable energy change during the rupture of intermolecular hydrogen bonds.

According to discussion in Section II, this center can be a negative charge arising in I. Apparently, the reaction is not synchronous, yet one can hardly estimate a true degree of charge separation.

Attention must be drawn to one more aspect of I formation. $Pd_3(OAc)_6$ species is known to have a cyclic structure [30] with all acetato ligands being bridging. So Pd(II) vinylation requires either an attack of olefin on the fifth coordination site of Pd(II), or a cleavage of, at least, one acetato bridge. A conclusion that Pd(II) solvation remains in the transition state is in better agreement with the latter proposal, since the fifths coordination sites are involved in a contact of Pd(II) with solvent. Thus, the interaction of $Pd_3(OAc)_6$ with styrene may be schematically represented as follows:



where X is an acetato ligand.

It is easily seen, that a combination of eqns. (9) an (10) gives eqn. (7). Neglecting $\delta\mu^{\circ}_{St}$ as insignificantly small we obtain:

$$\delta\Delta G^{\neq} \approx \delta\mu^{\neq} - \delta\mu^{\circ}_{Pd} =$$

$$3.88 - 0.1\pi^* + 0.069\ \mathrm{DN} - 0.13\ E_T$$

It follows from $\pi^* \leqslant 1$ that $0.1\pi^* \leqslant 0.1$, therefore:

$$\delta\Delta G^{\neq} \approx 3.9 + 0.069\ \mathrm{DN} - 0.13\ E_T \qquad (11)$$

On the other hand it follows from eqn. (7) that:

$$\delta\Delta G^{\neq} = \Delta G^{\neq} - \Delta G^{\neq}_{heptane} =$$

$$3.6 + 0.063\ \mathrm{DN} - 0.125\ E_T \qquad (12)$$

Equations (11) and (12) are almost equivalent. The above analysis shows, however, that the E_T contribution must be referred to the initial state and the DN contribution must be referred to the transition state.

Experimental

Materials

Pd(II) acetate was prepared as it is described in [11]. Styrene (Apolda, GDR) was passed through the silica-gel column before use. All solvents (except hexamethylphosphorictriamide) of a high purity (Reachim) were additionally purified before use by standard procedure [31, 32]. Hexamethylphosphorictriamide (Sigma) was used as received.

Kinetic Measurements

The general kinetic procedure was as follows. To a fresh prepared solution of Pd(II) acetate (1.0×10^{-3}–10×10^{-3} *M*) in 2–3 ml of solvent styrene (0.01–1.00 *M*) was added. The mixture was thermostated at an appropriate temperature within 20–55 °C. Reaction (1) was followed by measuring the initial rates of its product formation – E,E-1,4-diphenyl-1,3-butadiene. The aliquots were withdrawn periodically from the reaction mixture, diluted with dioxane and the concentration of E,E-1,4-diphenyl-1,3-butadiene was measured in this solution spectrophotometrically (Hitachi-356) at 330 nm (ϵ = 48000 M^{-1} cm^{-1}). At this wavelength absorptions of styrene, Pd(II) acetate, and reduced palladium were negligibly small.

Solubility measurements of Pd(II) acetate

Pd(II) acetate (0.2–0.3 g) was shaked in the thermostated (25 °C) vessel with 3–4 ml of a solvent. Aliquots were withdrawn periodically, filtered, and the filtrate was treated with 1.0 *M* HCl. The concentration of Pd(II) in the form $PdCl_4^{2-}$ was determined spectrophotometrically at 475 nm (ϵ = 131 M^{-1} cm^{-1}). After 2–3 h the concentration of Pd(II) in solution became constant and this concentration was thought to be equal to its solubility, S_{Pd}. S_{Pd} values are collected in Table IV.

Distribution of styrene between the polymer phase and the solvent

Divinylbenzene cross-linked polystyrene (Polysorb-1) (0.2 - 0.4 g) was shaked in the thermostated (25 °C) vessel with 5 ml of 0.17 *M* solution of styrene in a given solvent for 24 h. Then the polymer beads were separated from the solvent and transferred to 5 ml of pure dioxane. After shaking for 24 h the concentration of extracted styrene was measured spectrophotometrically at 292 nm (ϵ = 475 M^{-1} cm^{-1}). In preliminary experiments it was shown that 24 h is a sufficient time for the equilibrium distribution of styrene between a solution and a polymer to be achieved. Pure dioxane extracts practically all styrene, absorbed by the resin, so from the concentration of the extracted styrene one can calculate the quantity of styrene absorbed during the contact of the resin with 0.17 *M* styrene solution. A partition constant, P_{St}, was calculated as a ratio of styrene concentration in the resin (mmol/g) to that in the solution (mmol/ml). P_{St} values are summarized in Table IV. The ratio $P_{St}{}^{a}/P_{St}{}^{b} = P^{a,b}$ gives the partition constant of styrene between solvents 'a' and 'b'. To verify the reliability of this method one may compare obtained $P^{a,b}$ values with the directly measured partition constants for some pairs of immiscible solvents. For the pair heptane–DMSO, in particular, the directly measured $P^{a,b}$ was 0.83 and must be compared with $P^{a,b} = 0.75$ calculated from Table IV. For another pair heptane–acetonitrile, however, a discrepancy was more pronounced. The measured value was equal to 0.71 and the calculated one was 1.4.

The main source of systematic errors in determining P_{St} comes from a swelling of the resin. To take this factor into account we have measured P_{St} for benzene and acetone using Polysorb-2 resin additionally cross-linked by γ-irradiation. P_{St} values obtained 2.0 and 1.4 ml/g in acetone and benzene, respectively, are the same as in Table IV within the experimental error.

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