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Solvation Effects in the Dimerization of 2-Ethylprop-2-enal

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Abstract—Rate constants for dimerization of 2-ethylprop-2-enal in different solvents cannot be approximated using a single solvent parameter. This is possible only with the aid of multiparameter equations. Polar solvents characterized by a high cohesion energy density accelerate the process.

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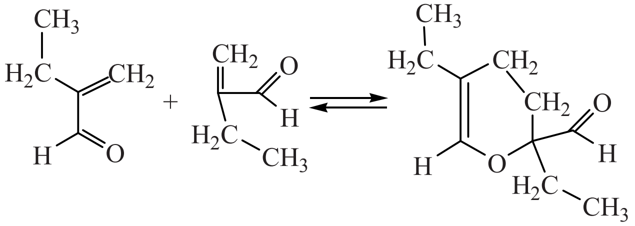
Properties of acrylic polymers strongly depend on the monomer structure. For example, extension of the hydrocarbon chain in alkylacrylates enhances elasticity and solubility of polymers derived therefrom. Acrylic monomers having cyclic substituents have been studied considerably more poorly. We examined dimerization of 2-ethylprop-2-enal leading to 2,5-diethyl-3,4-dihydro-2*H*-pyran-2-carbaldehyde. The procedure for carrying out this reaction was described in [1]. The resulting heterocyclic aldehyde was proposed for use as component for copolymerization with alkenes, dienes, and vinyl ethers. Such copolymers attract interest as materials for polygraphy and light-sensitive and laminating films [2–4].



We a view to elucidate the mechanism of dimerization of 2-ethylprop-2-enal we examined the kinetics of this process at 190°C in nine solvents characterized by different solvating abilities. The corresponding second-order rate constants are collected in table. The reaction was the slowest in dioxane, while the highest reaction rate was observed in aromatic solvents. Insofar as the available experimental data did not allow us to derive a distinct dependence of the rate constants upon particular solvent parameters, we tried to correlate them with the use of Koppel'–Pal'm six-parameter equation (1) which takes into consideration both specific and nonspecific solvation ability of solvents and their structure.

$$\log k = a_0 + a_1\frac{n^2-1}{n^2+2} + a_2\frac{\varepsilon-1}{2\varepsilon+1} + a_3B + a_4E_T + a_5\delta^2 + a_6V_{\mathrm{M}}. \qquad (1)$$

Equation (1) and calculations procedures were described in detail in our previous publications [5, 6]. Correlation of the data for all 9 solvents gave six-parameter equation with an unsatisfactorily poor multiple correlation coefficient (R = 0.794). However, exclusion of the most deviating data for only one solvent, carbon tetrachloride, gave a correlation with R = 0.999.

The significance of particular terms of Eq. (1) cannot be estimated from the pair correlation coefficients r, for the latter were very low (r = 0.1–0.4). Therefore, their significance was determined according to the IUPAC recommendations [7] via successive exclusion of particular terms and calculation of R for the resulting equation with a smaller number of terms. We thus revealed the solvent molar volume does not affect the reaction rate. Exclusion of the corresponding term reduced the R value only to 0.991. Nonspecific solvation related to solvent polarizability also turned out to be relatively insignificant. The relation between the reaction rate and solvent parameters can be described satisfactorily by four-parameter Eq. (2).

$$\log k = -1.578 + (4.956\pm0.538)f(\varepsilon) - (1.921\pm0.197)\times10^{-3}B - (0.144\pm0.019)E_T + (2.722\pm0.402)\times10^{-3}\delta^2, \qquad (2)$$

$$R\ 0.972,\ s\ \pm0.038\ N\ 8.$$

Experimental log *k* values for dimerization of 2-ethylprop-2-enal (190°C) and those calculated by Eq. (2)

Solvent	k, l mol^{-1} s^{-1}	log(k_{exp})	log(k_{calc})	Δ log k
DMSO	2.53×10^{-5}	–4.5969	–4.6227	–0.0258
Acetonitrile	3.06×10^{-5}	–4.5143	–4.4845	0.0298
1,4-Dioxane	1.08×10^{-5}	–4.9666	–4.9458	0.0208
Toluene	3.37×10^{-5}	–4.4724	–4.4698	0.0026
Benzene	3.47×10^{-5}	–4.4597	–4.5038	–0.0442
Tetrahydrofuran	2.93×10^{-5}	–4.5331	–4.5295	0.0036
Ethyl acetate	2.59×10^{-5}	–4.5867	–4.5255	0.0612
Methyl ethyl ketone	2.52×10^{-5}	–4.5986	–4.6467	–0.0481
CCl_4	1.80×10^{-5}	–4.7447	–4.2648	0.4799

Exclusion of any parameters from Eq. (2) completely destroys the correlation: the *R* value falls down to 0.4–0.8; here, log*k* is most sensitive to solvent basicity.

We can conclude that *n*-donor solvents capable of solvating the initial aldehyde in specific mode reduce the reaction rate, i.e., hamper dimerization. By contrast, increase in solvent polarity (which favors charge separation) accelerates the process. An indirect support for the above stated is the minimal reaction rate in nonpolar carbon tetrachloride which is incapable for specific solvation. The dimerization process is also favored by increase in the cohesion energy density. Presumably, self-association of solvent molecules gives rise to a cage accommodating the transition state leading to the dimeric product. Analogous positive cage effect is also observed in radical processes. The log*k* values calculated by Eq. (2) and their deviations from the experimental values are given in table. It is seen that Δlog*k* values generally do not exceed 2*s* (*s* = ±0.038; ethyl acetate, methyl ethyl ketone, benzene).

Taking into account chemical aspects of the process, the structure of initial aldehyde, specifically the size of the substituent therein, i.e., steric factor must be important. Therefore, we examined the kinetics of dimerization of a series substituted unsaturated aldehydes from acrolein to 2-butylprop-2-enal under similar conditions. As a result, the following rate constants *k* were found: 1.18×10^{-4} (acrolein), 4.33×10^{-5} (2-methylprop-2-enal), 3.45×10^{-5} (2-ethylprop-2-enal), and 1.7×10^{-5} l mol^{-1} s^{-1} (2-butylprop-2-enal). An acceptable but fairly poor correlation with the Hammett–Taft steric constant was obtained (*R* = 0.97). The correlation between log*k* and σ was even poorer (*R* = 0.93 against a recommended value of 0.95). On the other hand, two-parameter correlation was characterized by an *R* value of 0.989.

$$\log k = -4.32 + (0.46\pm0.17)\sigma^* + (0.62\pm0.14)E_S. \qquad (3)$$

We can state with some certainty that dimerization of unsaturated aldehydes is determined mainly by electronic properties of the substituents, though steric factor is also significant. As the size of the substituent increases, E_S value becomes negative, and the rate constant correspondingly decreases.

Dimerization of unsaturated aldehydes is a particular case of Diels–Alder reaction. Its mechanism has not been so far interpreted unambiguously. Three versions of the reaction were proposed. The first of these implies a two-step zwitterionic mechanism, according to which heterolytic formation of new C–C bond in the initial step gives rise to zwitterionic intermediate. The second mechanism also includes two steps; here, as in the first case, diradical intermediate is formed in the first step. The third version is one-step concerted mechanism involving cyclic transition state with six delocalized π-electrons [8].

It is commonly believed that Diels–Alder reactions follow one-step concerted mechanism; however, some authors presume initial formation of one C–C bond, followed by generation of diradical species, on the basis of quantum-chemical calculations [9].

In our case, considerable solvent effect on the reaction rate, as well as the values of activation parameters found for the dimerization process in the bulk (solvent-free) [1], allowed us to presume one-step concerted dimerization mechanism. This is also supported by the failure to accomplish photochemical dimerization of 2-ethylprop-2-enal under UV irradiation (80 W) in the temperature range from 20 to 70°C both in the presence and in the absence of initiators (acetophenone, benzil, 2,2-dimethyl-2-phenylacetophenone). In all cases, no dimerization product was detected, i.e., the dimerization does not involve intermediate formation of radical species.

Our results show that such solvents as benzene, toluene, acetonitrile, and tetrahydrofuran accelerate dimerization of 2-ethylprop-2-enal. From the practical viewpoint, benzene is the best solvent (it is relatively cheap and accessible). Furthermore, the boiling point of benzene (80°C) approaches that of 2-ethylprop-2-enal (92°C), so that there is no need of separating them after isolation of the dimer, and the mixture can be reused.

EXPERIMENTAL

Initial aldehydes were purified by fractional distillation before use; their physical constants were consistent with published data. The solvents used were purified by standard procedure [10].

Kinetic experiments were performed in sealed glass ampules at 190°C according to the procedure described in [11]. Mixtures containing 0.01 mol of the initial aldehyde and 0.05 mol of the corresponding solvent were prepared, and hydroquinone was added. A 2-ml ampule was charged with 0.5 ml of the above mixture, purged with nitrogen, sealed, and heated in a thermostat. At definite time intervals, the ampule was withdrawn, quickly cooled, and opened, and the mixture was analyzed by gas–liquid chromatography on a GCHF 18.3 instrument coupled with an IBM PC-286; thermal conductivity detector, detector current 140 mA; stainless steel column, 2 m×4 mm, packed with 3% of XE-60 on Chromaton N Super (0.16–0.20 mm); oven temperature 145°C, detector temperature 185°C, injector temperature 200°C; carrier gas hydrogen, flow rate 25 ml min^{-1}; sample volume 0.5–1 μl; quantitation was performed by the standard addition technique. The rate constants were calculated using second-order equation (4).

$$2k\,\tau = 1/c - 1/c_0. \tag{4}$$

Here, c_0 is the initial concentration of 2-ethylprop-2-enal (1.7–2 M, depending on the solvent), c is the current concentration of 2-ethylprop-2-enal (M), and τ is the reaction time (s). The progress of reactions was monitored up to 80% conversion of the initial aldehyde. The rate constants given in table were averaged by the least-squares procedure.

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