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Solvent effect on the decarbonylation of acyl radicals

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The rate constant k_{co} of decarbonylation of phenylacetyl and 2-hydroxy-2-methylpropanoyl radicals, generated by photolysis of dibenzyl ketone and 2,4-dihydroxy-2,4-dimethyl-3-pentanone, was measured in a number of solvents over a wide temperature range. The pre-exponential factors A and activation energies E_a were found for all solvents. The rate constant of phenylacetyl decarbonylation decreases with the increase of the solvent relative permittivity ε , but increases in protic solvents. The results of quantum chemistry calculations confirm the mutual cancellation of the contributions of specific and nonspecific solvations to the activation energy of the decarbonylation reaction in alcohols. For the 2-hydroxy-2-methylpropanoyl radical, the solvent effect on the decarbonylation rate constant is very small.

Introduction

Solvent effects on the mechanism and rate constants of chemical reactions have attracted the attention of many physical chemists. A recent book by Reichardt¹ includes more than 2300 references on this subject. The solvent effect is most pronounced in reactions involving cations and anions. In this case, the change of reaction rate constants in different solvents can reach many orders of magnitude,² and reaction mechanisms can change drastically.

The influence of solvent on radical reactions is most significant when the radicals are charged, or when polar radicals participate in bimolecular reactions.¹ The influence of solvent on the monomolecular reactions of polar radicals is considered as very weak, and even negligible in the case of nonpolar radicals. In particular, the decarbonylation of the phenylacetyl radical was suggested as a "chemical clock", *i.e.* a reaction for which the rate constant does not depend on the solvent, and which can be used for the determination of the absolute rate constants of parallel reactions.^{3–5} However, recently a solvent effect has been revealed in the reactions of β -scission of some alkoxyl radicals^{6–9} and of decarbonylation of acyl radicals.^{10,11}

It was shown that the rate constant of β -scission of alkoxyl radicals increases with the increase in solvent polarity. This effect can be accounted for as follows: polar solvents stabilize the transition state for fragmentation more strongly than the initial radical. Thus, in polar solvents the activation energy of the reaction decreases, and the rate constant increases. Both the solvent polarity and its ability for hydrogen bonding accelerate the rate constant of β -scission. A good linear relationship was found between the commonly used solvent parameter^{1,12} $E_{\rm T}(30)$ and the logarithm of the rate constant for β -scission of cumyloxyl⁶ and *tert*-butoxyl⁹ radicals.

In the present work, the rate constants of the decarbonylation reaction of phenylacetyl and 2-hydroxy-2-methylpropanoyl radicals have been measured in a number of solvents over a wide temperature range. The main goal of this work is the quantitative analysis of the influence of solvent polarity and hydrogen bonding on the rate constant of radical fragmentation.

Experimental

Materials

All solvents used in this work were doubly distilled. 2,4-Dihydroxy-2,4-dimethyl-3-pentanone was synthesized following ref. 13 and purified by distillation. Dibenzyl ketone (Aldrich) was used as received.

Apparatus

A detailed description of the laser flash photolysis equipment has been published earlier.^{3,14} Solutions in a rectangular cell (10 mm \times 10 mm) were irradiated with a Lambda Physik EMG 101 excimer laser (308 nm, pulse energy up to 100 mJ, pulse duration 15 ns). The dimensions of the laser beam at the front of the cell were 3 mm \times 8 mm. The monitoring system includes a DKSh-120 xenon short-arc lamp connected to a high current pulser, two synchronously operating monochromators, a Hamamatsu R955 photomultiplier, and a LeCroy 9310A digitizer. All solutions were purged with argon for 15 min prior to, and during, irradiation.

Computational methods

Radical geometry optimization and transition state search were performed at the B3LYP¹⁵ level of theory using the 6-31G* basis set. The nature of the stationary point (*i.e.*, either minimum or transition state) was determined by calculating the vibrational frequencies, and the unscaled frequencies were used to obtain corrections for the zero-point vibrational energies. Free energies of solvation of radicals and transition states were calculated using the PCM model.¹⁶ Geometries and heats of formation of radicals, transition states and their complexes with methanol were calculated also by semi-empirical PM3 method.¹⁷ All calculations were performed using the GAUSSIAN98 program.¹⁸

Results

The phenylacetyl and 2-hydroxy-2-methylpropanoyl radicals were generated by the laser flash photolysis (LFP) of dibenzyl ketone (DBK) and 2,4-dihydroxy-2,4-dimethyl-3-pentanone (DHDMP), respectively. These reactions have been studied previously^{3,4,10,19-41} and can be described by the scheme:

$$R_{2}CO \xrightarrow{h\nu} R_{2}CO (S_{1}) \xrightarrow{<10^{-8} \text{ s}} R_{2}CO (T_{1})$$
(1)

$$R_2 CO (T_1) \xrightarrow{<10^{-9} s} \dot{RCO} + \dot{R}$$
(2)

$$\dot{RCO} \xrightarrow{k_{CO}} \dot{R} + CO$$
(3)

$$2R\dot{C}O \longrightarrow \text{products}$$
 (4)

$$2\dot{R} \xrightarrow{2k_2} \text{products}$$
 (5)

$$\dot{RCO} + \dot{R} \xrightarrow{x_x} products$$
 (6)

where R stands for $PhCH_2$ (LFP of DBK) and for $(CH_3)_2COH$ (LFP of DHDMP).

The absorption spectra of benzyl PhCH₂ and ketyl $(CH_3)_2COH$ radicals, formed in these reactions, were published earlier. Benzyl has absorption bands with maxima at 260 and 314 nm,^{10,24,42} whereas the absorption of ketyl radical in the near-UV region gradually increases toward short wavelengths.^{11,43–46} The transient absorption kinetics was measured at 314 nm in the LFP of DBK, and at 270 nm in the LFP of DHDMP.

An example in Fig. 1 shows the kinetic traces obtained by the LFP of DBK in three solvents at room temperature. The observed kinetics reflects the evolution of benzyl radical according to the reaction scheme (1)-(6): the initial absorption jump corresponds to the generation of benzyl radicals in the geminate reaction (2) followed by benzyl radical formation due to decarbonylation of phenylacetyl (3). Further signal decrease corresponds to the radical decay in the termination reactions (4)-(6). At the minimal laser energies used (about 1 mJ per pulse) the reactions of radical termination become much slower than decarbonylation, and the rate of the signal growth practically coincides with the rate of the reaction (3). It can be readily seen that the decarbonylation of the phenylacetyl radical is fastest in the nonpolar hexane and slowest in the polar aprotic acetonitrile.

Decarbonylation of the 2-hydroxy-2-methylpropanoyl radical at ambient temperature is too fast to be measured by conventional nanosecond flash photolysis, but at lower temperatures traces similar to those shown in Fig. 1 were observed.

Since the reactions of radical termination (4)–(6) are diffusion controlled, and the radicals are of similar size, we can use the approximation³⁹ $2k_t = 2k_1 \approx 2k_2 \approx k_x$. In this case, the kinetics of radical formation and decay can be described by eqns. (7) and (8):

$$\frac{\mathrm{d}[\dot{\mathrm{R}}]}{\mathrm{d}t} = k_{\mathrm{CO}}[\mathrm{R}\dot{\mathrm{C}}\mathrm{O}] - 2k_{\mathrm{t}}[\dot{\mathrm{R}}]^2 - 2k_{\mathrm{t}}[\dot{\mathrm{R}}][\mathrm{R}\dot{\mathrm{C}}\mathrm{O}] \qquad(7)$$

$$\frac{\mathrm{d}[\mathrm{R}\dot{\mathrm{CO}}]}{\mathrm{d}t} = -k_{\mathrm{CO}}[\mathrm{R}\dot{\mathrm{CO}}] - 2k_{\mathrm{t}}[\mathrm{R}\dot{\mathrm{CO}}]^2 - 2k_{\mathrm{t}}[\dot{\mathrm{R}}][\mathrm{R}\dot{\mathrm{CO}}] \quad (8)$$

Solution of this system yields the time dependence of benzyl (ketyl) radical concentration:⁴⁷

$$[\dot{\mathbf{R}}] = R_0 \{2 - \exp(-k_{\rm CO} t)\} / (1 + 4k_{\rm t} R_0 t)$$
(9)

where R_0 is the initial radical concentration, $R_0 = [\dot{R}](t = 0)$. Determination of the decarbonylation rate constant k_{CO} was



Fig. 1 Transient absorption kinetics of benzyl radicals (314 nm) in hexane (1), methanol (2) and acetonitrile (3) at room temperature. Bold lines show the best fit to eqn. (9).

performed in the following way. At every given temperature three or four kinetic traces were obtained with the laser power varying between 1 and 10 mJ per pulse. Typical concentration of DBK was 3×10^{-3} M, and 2×10^{-2} M for DHDMP. Thus, the initial radical concentration in the intersection of the exciting and monitoring beams varied in the range from 2×10^{-6} M to 2×10^{-5} M in the LFP of DBK and in the range from 2×10^{-5} M to 2×10^{-4} M for DHDMP. The experimental traces were treated according to eqn. (9). The absorption coefficients $6500 \text{ M}^{-1} \text{ cm}^{-1}$ for phenyl-acetyl^{10,24,42} and $860 \text{ M}^{-1} \text{ cm}^{-1}$ for 2-hydroxy-2methylpropanoyl¹¹ radicals were taken from the literature, whereas the rate constants k_{co} and k_t and the initial radical concentration R_0 were fitting parameters. The deviations of the calculated $k_{\rm CO}$ values within each set of data usually did not exceed 5-7%. Some of the simulations are shown in Fig. 1 (the bold line corresponds to the calculated curves).

Results of the Arrhenius treatment of the decarbonylation rate constants in three solvents are shown in Fig. 2 (LFP of DBK) and Fig. 3 (LFP of DHDMP). Similar temperature dependences were obtained for other solvents as well. As one can see, the experimental data show good linear dependences in Arrhenius coordinates, which allowed for the determination of pre-exponential factors (A) and activation energies (E_a). The Arrhenius parameters are collected in Tables 1 and 2 for the decarbonylation of phenylacetyl and 2-hydroxy-2-methylpropanoyl radicals, respectively. The tables also include the values of k_{CO} at ambient temperature, which for phenylacetyl are in a good agreement with the previous reports.^{4,5,10} For



Fig. 2 Arrhenius plots for the rate constant of phenylacetyl decarbonylation in hexane (squares), isopropanol (triangles) and acetonitrile (circles).

Table 1 Rate constants k_{CO} of decarbonylation of phenylacetyl radicals at ambient temperature and Arrhenius parameters for k_{CO} in various solvents

Solvent	$\frac{\varepsilon-1}{2\varepsilon+1}$	$E_{\mathrm{T}}^{\mathrm{N}}$	$k_{\rm CO}(295 {\rm ~K})/{\rm s}^{-1}$	$\log(A/s^{-1})$	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$
Hexane	0.188	0.009	$(4.5 \pm 0.3) \times 10^{6}$	12.2 ± 0.6	31.5 ± 1.1
Chloroform	0.356	0.259	$(3.0 \pm 0.3) \times 10^6$	12.9 ± 0.6	36.4 ± 1.4
Acetic acid	0.388	0.648	$(2.0 \pm 0.2) \times 10^{6}$	11.7 ± 0.6	30.5 ± 1.2
Dichloromethane	0.420	0.309	$(1.9 \pm 0.1) \times 10^{6}$	13.1 ± 0.5	38.3 ± 1.4
Isopropanol	0.460	0.546	$(2.6 \pm 0.2) \times 10^{6}$	12.5 ± 0.6	34.2 ± 1.5
Ethanol	0.470	0.654	$(2.4 \pm 0.2) \times 10^{6}$	11.5 ± 0.4	28.9 ± 0.9
Methanol	0.477	0.762	$(2.2 \pm 0.2) \times 10^{6}$	12.1 ± 0.6	32.2 ± 1.3
Acetonitrile	0.480	0.460	$(1.4 \pm 0.1) \times 10^{6}$	13.1 ± 0.7	39.6 ± 1.5



Fig. 3 Arrhenius plots for the rate constant of 2-hydroxy-2-methylpropanoyl decarbonylation in methanol (squares), ethyl acetate (triangles) and acetonitrile (circles).



Fig. 4 Correlation between Kirkwood's parameter $(\varepsilon - 1)/(2\varepsilon + 1)$ and the activation energy of phenylacetyl decarbonylation in different solvents.

the 2-hydroxy-2-methylpropanoyl radical these values are estimated by extrapolation of the low-temperature data to 295 K.

Discussion

The results obtained for the decarbonylation of the phenylacetyl radical agree qualitatively with the earlier conclusions¹⁰ that the decarbonylation rate constant decreases in polar solvents. According to the transition state theory, the influence of media on a rate constant is due to the difference in the free energies of solvation of an initial radical and a transition state. If the initial radical is more polar than the transition state, the difference in the free energy of solvation increases with increase in the solvent polarity. That results in the increase of the activation energy $E_{\rm a}$ and decrease of the rate constant in polar solvents as compared to nonpolar ones. Thus, the experimental results have a simple qualitative explanation: since in the course of fragmentation the polar phenylacetyl radical transforms into the nonpolar benzyl radical and CO molecule, the transition state for the decarbonylation reaction should also be less polar than the initial radical.

In the simplest Onsager model, the solvent polarity can be characterized by the dielectric constant ε , and the solvent effect on the reaction rate constant k can be described with the use of Kirkwood's formula:¹

$$\ln(k) - \ln(k_0) = -\frac{\Delta G_{solv}^{\ddagger}}{RT} = -\frac{1}{4\pi\varepsilon_0} \frac{N_A}{RT} \frac{\varepsilon - 1}{2\varepsilon + 1} \left(\frac{\mu_a^2}{r_a^3} - \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3}\right),$$
(10)

where k_0 corresponds to the hypothetical solvent with $\varepsilon = 1$, μ_a , μ_{\ddagger} , r_a and r_{\ddagger} are the dipole moments and the radii of the initial radical and the transition state, respectively. According to this formula, the change in activation energy of the reaction is proportional to the parameter $(\varepsilon - 1)/(2\varepsilon + 1)$.

Fig. 4 shows the plot of the activation energies of the decarbonylation reaction of the phenylacetyl radical in different solvents vs. $(\varepsilon - 1)/(2\varepsilon + 1)$. A good linear correlation can be found only for aprotic solvents, whereas the data for alcohols and acetic acid lay far away from the values expected

Table 2 Rate constants k_{co} of decarbonylation of 2-hydroxy-2-methylpropanoyl radicals at room temperature and Arrhenius parameters for k_{co} in various solvents

Solvent	$\frac{\varepsilon - 1}{2\varepsilon + 1}$	$E_{\mathrm{T}}^{\mathbf{N}}$	$k_{\rm CO}(295 {\rm ~K})/{\rm s}^{-1}$	$\log(A/s^{-1})$	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$
Methylcyclopentane Diethyl ether Ethyl acetate Methanol Acetonitrile	0.198 0.341 0.385 0.477 0.480	0.010 0.117 0.228 0.762 0.460	$\begin{array}{l} 4.4 \times 10^{7} \\ 1.1 \times 10^{8} \\ 8.2 \times 10^{7} \\ 6.9 \times 10^{7} \\ 4.1 \times 10^{7} \end{array}$	$\begin{array}{c} 11.2 \pm 1.6 \\ 12.0 \pm 0.5 \\ 12.1 \pm 0.4 \\ 11.7 \pm 0.4 \\ 11.3 \pm 0.9 \end{array}$	$\begin{array}{c} 20.3 \pm 1.8 \\ 22.5 \pm 1.1 \\ 23.8 \pm 1.2 \\ 21.9 \pm 0.9 \\ 21.0 \pm 0.9 \end{array}$



Fig. 5 Correlation between parameter $E_{\rm T}^{\rm N}$ and the activation energy of phenylacetyl decarbonylation in different solvents.

according to formula (10). That is not surprising since the Kirkwood formula is oversimplified and takes into account only electrostatic interactions between solvent and solute, leaving aside all other interactions, most importantly, hydrogen bonding. Besides, the Onsager model treats the molecule as a sphere with a point dipole in the center and does not take into account the real shape of the molecule and the charge distribution.

The other commonly used approach to describe the solvent effect on reaction rate constants is the use of empirical parameters characterizing the solvent polarity, among which the most popular is the Dimroth's $E_{\rm T}$ scale.¹ Empirical parameters take into account not only the electrostatic interactions, but also the specific interactions between solute and solvents. Indeed, a good linear correlation has been found between solvent parameter $E_{\rm T}(30)$ and the logarithm of the rate constant for some reactions, in particular for the reaction of β -scission of alkoxyl radicals.^{6,9}

The dependence of the phenylacetyl decarbonylation rate constant on the parameter E_T^N is shown in Fig. 5. It is obvious that a linear correlation can be found only for aprotic solvents, as well as with the use of Kirkwood's formula.

One should note that the parameter E_T^N is proportional to the energy of the electronic transition of a standard compound in different solvents,¹ and it grows with the increase of both solvent relative permittivity and its ability for hydrogen bonding. Thus, a linear correlation between $E_{\rm T}^{\rm N}$ and the reaction activation energy can take place only if the electrostatic interactions and hydrogen bonding influence the reaction rate constant in a similar manner. It is possible that the initial radical is more polar than the transition state, whereas the hydrogen bonding stabilizes the transition state more strongly than the initial radical. In this case the mutual compensation of specific and nonspecific solvation can occur. Most likely, just this situation takes place in the case of phenylacetyl decarbonylation. In order to confirm this assumption, we performed quantum chemical calculations of the solvent effect on the barrier to decarbonylation of the phenylacetyl radical.

The geometries of the phenylacetyl radical and of the transition state were optimized at the B3LYP/6-31G* level. The length of the R–CO bond, which cleaves during the reaction, in the transition state was found to be about 0.5 Å longer than that in the initial radical, and the lengths of the other bonds change insignificantly (Fig. 6). Also, redistribution of spin density from carbonyl group to methylene group takes place. The energy difference between the transition state and the initial radical is 37.9 kJ mol⁻¹ or 29.9 kJ mol⁻¹ with zeropoint energy (ZPE) correction, and the enthalpy difference is equal to 30.4 kJ mol⁻¹. The latter values are in very good agreement with the experimental activation energy in nonpolar solvent hexane (31.5 ± 0.5 kJ mol⁻¹). The dipole moment calculated using the B3LYP/ $6-31G^*$ method changes from 2.3 D in phenylacetyl to 1.6 D in the transition state. PM3 calculations also demonstrate a similar decrease of the dipole moment in the transition state. Thus, the electrostatic interactions with solvents should increase the activation barrier and decrease the decarbonylation rate constant, which agrees qualitatively with the experimental findings (see data for aprotic solvents in Table 1 and Figs. 4 and 5).

To account quantitatively for the influence of the electrostatic interactions with solvent on the rate constant, we used the more sophisticated polarized continuum model (PCM),¹⁶ which takes into account the more realistic shape of a solvent cavity and real charge distribution in a radical. Free energies of solvation were calculated in two solvents, hexane and acetonitrile. The calculated difference in the free energy of activation in these two solvents $\Delta G_{ACN}^{\ddagger} - \Delta G_{hex}^{\ddagger} = 4.2 \text{ kJ mol}^{-1}$ is in a fairly good agreement with the experimental data.

The influence of hydrogen bonding on the reaction rate constant was calculated taking into account the difference in the enthalpies of complex formation of the radical and the transition state with solvent molecules. Methanol was used as a typical molecule forming hydrogen bonds. The heat of complex formation with the radical $(7.2 \text{ kJ mol}^{-1})$ was noticeably lower than that with the transition state (12.9 kJ mol⁻¹). Thus, the stabilization of the transition state by hydrogen bonding is stronger than the stabilization of the initial radical. This result confirms that hydrogen bonding, in contrast to nonspecific solvation, decreases the activation energy and accelerates the rate of the decarbonylation. The calculated effects of electrostatic interactions and hydrogen bonding on the decarbonylation rate constant are of similar scales and of different signs in the case of typical protic solvent methanol, which is in good agreement with the experimental findings: the activation energies is alcohols and in acetic acid are close to that in nonpolar solvent hexane (Table 1).

Thus, the quantum chemical calculations confirm the hypothesis about mutual compensation of effects of specific and nonspecific solvation on the rate constant of decarbonylation of the phenylacetyl radical.

Comparison of Tables 1 and 2 shows that, although 2hydroxy-2-methylpropanoyl and phenylacetyl radicals have similar dipole moments, the solvent effect on the rate constant of decarbonylation of the former is much smaller than that of the latter. The qualitative explanation of this is that both polarity and hydrogen bonding abilities of the 2-hydroxy-2methylpropanoyl are associated with the hydroxy group, present in the initial radical as well as in the transition state and in the ketyl radical formed after decarbonylation. The quantum chemical calculations confirm this statement.

Elongation of the R–CO bond in the transition state of the 2-hydroxy-2-methylpropanoyl radical is even larger than that for phenylacetyl, whereas the redistributions of the spin densities in both radicals are similar (Fig. 7). The energy difference



Fig. 6 Geometries and spin density distribution in the phenylacetyl radical (R) and in the transition state of its decarbonylation (TS).



Fig. 7 Geometries and spin density distribution in the 2-hydroxy-2methylpropanoyl radical (left) and in the transition state of its decarbonylation (right).

between the transition state and the initial radical is 32.5 kJ mol⁻¹ or 24.4 kJ mol⁻¹ with ZPE correction. The latter value is in fairly good agreement with the experimental activation energy (20.3 ± 0.9 kJ mol⁻¹ in hexane). In contrast to phenylacetyl, the dipole moment of the transition state (2.1 D) is a little larger than that of the initial radical (1.8 D). The difference in the free energy of activation in acetonitrile and hexane, calculated using the PCM model, is very small: $\Delta G_{\rm ACN}^{\dagger} - \Delta G_{\rm hex}^{\dagger} = -0.7$ kJ mol⁻¹. This theoretical result is in good agreement with the experimental finding that the activation energies of the reaction in hexane and acetonitrile are very close.

We also performed calculations of the enthalpies of complex formation of the initial radical and transition state with methanol, using the PM3 model. Two types of complex can be formed: (a) an alcohol is a hydrogen donor; (b) an alcohol is a hydrogen acceptor (see Fig. 8).

In case (a) the heat of complex formation with the radical $(7.0 \text{ kJ mol}^{-1})$ is a little larger than that with the transition state (6.2 kJ mol⁻¹). The heat of complex formation is much higher in the case of (b) type complex: 17.8 kJ mol^{-1} with the initial radical and 13.4 kJ mol^{-1} with the transition state. Therefore the activation energy should increase and the rate constant decrease for the decarbonylation of the 2-hydroxy-2-methylpropanoyl radical in solvents forming hydrogen bonds due to electron pair donation. Indeed, the activation energy of decarbonylation is a little higher in ether and ethyl acetate, but the effect is very small.

Experiment (Tables 1 and 2) and calculations show that the activation energies of the decarbonylation reaction of the phenylacetyl radical $(30-40 \text{ kJ mol}^{-1})$ are significantly higher than those of the 2-hydroxy-2-methylpropanoyl radical $(20-24 \text{ kJ mol}^{-1})$. We also calculated the energy difference between the initial radicals and final products of the decarbonylation reaction (Table 3). Opposite to the commonly valid relationship between the enthalpies of activation and reaction,⁴⁸ the thermally neutral reaction has higher activation energy than the endothermic one (Table 3).

Earlier the relationship between $log(k_{CO})$ and the enthalpy of the decarbonylation reaction was considered by Vollenweider and Paul.⁴⁹ A usual linear correlation has been found for all acyl radicals except phenyl-containing ones. However, the



Fig. 8 Structures of the two types of complexes of 2-hydroxy-2methylpropanoyl radical with methanol.

experimental data used in this study⁴⁹ were taken from different sources and were obtained in different experimental conditions. As a result, data scatter for some radicals exceeded two orders of magnitude. Besides, the enthalpy of R–CO bond cleavage was estimated in a relatively rough way.

We have performed B3LYP/6-31G* calculations of the reaction enthalpy and the barrier to the decarbonylation of some acyl radicals. The results are presented in Table 3. First of all, we have to mark a very good agreement between our calculations and estimations of the reaction enthalpies made by Vollenweider and Paul.⁴⁹ Second, the calculated reaction barriers coincide well with the experimental values of the activation energies for nonpolar solvents.

Finally, the deviation from the linear relationship between bond dissociation enthalpy and reaction barrier for the phenylacetyl radical becomes apparent (Fig. 9). The deviations for phenyl-containing radicals can be explained in the following way. The reaction coordinate for this reaction is a combination of the C-C bond stretch and libration motion of the methylene carbon. The barrier heights for this reaction are mainly determined by stretching of the C-C bond and are similar for phenylacetyl and 2-hydroxy-2-methylpropanoyl radicals. In the transition states $R_1R_2R_3C$ fragments are pyramidal and in the case of PhCH₂ hydrogen atoms are 22° out of the phenyl plane. When moving along the decaying branch of the phenylacetyl reaction coordinate a large part of the whole energy decrease (16.4 kJ mol⁻¹) is associated with the relaxation of PhCH₂ geometry (14 kJ mol⁻¹). Note that the difference in ZPE between the products and the transition state is 15.5 kJ mol⁻¹. The energy decrease due to the relaxation of (CH₃)₂COH or CH₃ radicals is very small (3-4 kJ mol^{-1}). Therefore we conclude that the reason for the deviation from the linear relationship for phenyl-containing acetyl radicals⁴⁹ is the aromaticity of benzyl radicals (PhCR₁ R_2).



Fig. 9 Data of quantum chemical calculations by the B3LYP/6-31G* method: dependence of the reaction barrier (ΔE^{\ddagger}) on the energy difference (ΔE_0) between product (R + CO) and reactant (RCO) (corrected for ZPE).

Table 3 Data of quantum chemical calculations of the bond dissociation enthalpy $[\Delta H(R-CO)]$, the reaction barrier to dissociation (ΔE^{\ddagger}) , the enthalpy of activation at 298 K (ΔH^{\ddagger}), the C···CO bond length in the transition state, and the dipole moment in the initial (d_{rad}) and transition (d_{rs}) states

	$\Delta H(R-CO)/kJ \text{ mol}^{-1}$		B3LYP/6-31G* calculations				
R	B3LYP/6-31G*	Ref. 49	$\Delta E^{\ddagger}(\Delta H^{\ddagger})/kJ \text{ mol}^{-1}$	R(C···CO)/A	$d_{\rm rad}/{ m D}$	$d_{\rm TS}/{\rm D}$	
Ph-CH ₂	-2.1	-6 ± 2	29.8(30.4)	2.052	2.3	1.6	
HO(CH ₃) ₂ C	21.7	18 ± 8	24.3(26.0)	2.134	1.8	2.1	
(CH ₃) ₃ C	25.3	25 ± 5	36.3(38.0)	2.189	2.5	1.8	
C ₂ H ₅	48.9	43	59.2(61.5)	2.300	2.5	1.4	
CH,	61.8	61	73.3(75.8)	2.347	2.4	1.0	
Ph	117.7	109	_ ` `	—	3.5	_	

Conclusion

In the present paper, the importance of the solvent effect on the rate constant of acyl radical decarbonylation has been confirmed. It has been shown for the first time that the electrostatic interactions with solvent and hydrogen bonding can influence this reaction in different ways: the decarbonylation of phenylacetyl proceeds more slowly in polar solvents, whereas hydrogen bonding decreases the activation barrier and increases the reaction rate constant. It was also shown that the scale of the solvent effect is determined by the change of the radical polarity in the course of the reaction rather than by radical polarity itself: the solvent effect for phenylacetyl is much more pronounced than that for the 2-hydroxy-2-methylpropanoyl radical of similar polarity. For most acyl radicals a linear relationship exists between the enthalpy of the reaction of decarbonylation and the barrier to the reaction. Deviations from this linear dependence, found for phenyl-containing radicals, can be explained as the result of pronounced energy decrease due to the relaxation of $PhCR_1R_2$ radical structure.

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