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Effect of medium on the rate constant of decarbonylation of phenylacetyl radical

Yu. P. Tsentalovich,[a]★ O. A. Kurnysheva,[a,b] and N. P. Gritsan[b,c]

[a]*International Tomography Center, Siberian Branch of the Russian Academy of Sciences,*
3a ul. Institutskaya, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 33 1399. E-mail: yura@tomo.nsc.ru
[b]*Novosibirsk State University,*
2 ul. Pirogova, 630090 Novosibirsk, Russian Federation
[c]*Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences,*
3 ul. Institutskaya, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 2350. E-mail: gritsan@ns.kinetics.nsc.ru

The rate constant k_{CO} of decarbonylation of phenylacetyl radicals generated by photolysis of dibenzyl ketone was measured by laser flash photolysis technique in six solvents in a wide temperature range. The pre-exponential factors A and activation energies E_a of decarbonylation were found for all solvents. The k_{CO} value decreases with an increase in the dielectric constant ε of the solvent, whereas an increase in the ability of the solvent for hydrogen bonding increases k_{CO}. The results of quantum-chemical calculations confirm the mutual compensation of the contributions of specific and nonspecific solvations to the activation energy of decarbonylation in alcohols.

Key words: laser flash photolysis, radical fragmentation, decarbonylation, phenylacetyl radical, quantum-chemical calculations.

It has been considered for a long time that the rate constants of fragmentation of neutral radicals in a solution are virtually independent of the solvent nature.[1] For example, the decarbonylation of phenylacetyl radicals[2—4] was proposed to be used as a "chemical clock" for the quantitative determination of the absolute rates of the competitive reactions. The authors of recent works reported an increase in the reaction rates of β-scission of alkoxyl radicals[5—9] and a decrease in the rate of carbonylation of acyl radicals[10,11] in polar solvents.

The influence of the medium on the decarbonylation rate of phenylacetyl radicals has previously[10] been studied only at room temperature. It seems reasonable to find the activation energy and pre-exponential factor of these reaction rates in various solvents and examine the influence of the medium on these parameters in a quantitative way. In this work, laser flash photolysis measurements were carried out to determine the rate constants of decarbonylation of phenylacetyl radicals generated by photolysis of dibenzyl ketone in a wide range of temperatures for a series of solvents. The influence of the dielectric properties of the solvents and their ability for hydrogen bonding on the rate constant and activation energy of this reaction was examined.

Experimental

Materials. Solvents were purified by repeated distillation. Dibenzyl ketone («Aldrich») was used as received.

Pulse photolysis. A laser pulse photolysis technique has been described previously.[8,12] A solution circulating through a rectangular quartz cell 10×3 mm in size using a flow system was irradiated with an XeCl-excimer pulse laser (Lambda Physik EMG 101, 308 nm, pulse energy up to 100 mJ, pulse duration 15—20 ns). The monitoring system included a DKsSh-150 xenon short-arc lamp (pulse duration 2 ms, size of the detection beam 2×3 mm), two synchronically monitored monochromators, a Hamamatsu R955 photomultiplier, a digital two-channel oscilloscope with an 11-bit analog-to-digital converter (LeCroy 9310A, 400 MHz, time resolution 10 ns), and a system of filters and shutters. All solutions were purged with argon to remove oxygen from the system prior to use and during irradiation. The temperature of samples was varied within the 248—347 K interval by a thermostabilized nitrogen flow and measured by a thermocouple.

Quantum-chemical calculations of the geometry and heat of formation of the phenylacetyl radical, transition state, and their complexes with alcohols were performed by the PM3 method[13] using the MNDO 92 program (the next version of the MNDO 85 program[14]). In addition, the geometry, electronic structure, and solvation energy of the initial radical and transition state were calculated by the density functional theory in the variant of the B3LYP hybrid method[15] using the GAUSSIAN 98 program.[16] The 6-31G* basis set was used in all cases. The polarized continuum model (PCM, Tomasi model)[17] was used to calculate the solvation energy.

Results and Discussion

The mechanism of photolysis of dibenzyl ketone R_2CO (where R = $PhCH_2$) is well studied[18] and described by the following reactions:

$$R_2CO \xrightarrow{h\nu} R_2CO\ (S_1) \xrightarrow{<10^{-8}\ s} R_2CO\ (T_1) \qquad (1)$$

$$R_2CO\ (T_1) \xrightarrow{<10^{-9}\ s} RCO + R \qquad (2)$$

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

$$2\,\mathrm{RCO} \xrightarrow{2k_1} \text{Products} \qquad (4)$$

$$2\,\mathrm{R} \xrightarrow{2k_2} \text{Products} \qquad (5)$$

$$\mathrm{RCO + R} \xrightarrow{k_x} \text{Products} \qquad (6)$$

Since the recombination reactions of the radicals are controlled by diffusion and the size of the radicals is approximately equal, we can use the approximation[19] $2k_t = 2k_1 \approx 2k_2 \approx k_x$. In this case, the kinetics of formation and decay of the benzyl and phenylacetyl radicals is described by the system of Eqs. (7) and (8).

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

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

The solution of this system gives the the concentration of benzyl radicals $[\mathrm{R}^{\bullet}]$ as a function of time[20]

$$[\mathrm{R}^{\bullet}] = \mathrm{R}_0(2 - \exp(-k_{\mathrm{CO}}t))/(1 + 4k_t\mathrm{R}_0 t), \qquad (9)$$

where R_0 is the initial concentration of benzyl radicals.

Transient absorption kinetics of the benzyl radical detected at the absorption maximum (λ = 314 nm)[10] is presented in Fig. 1. The instant increase in the absorption immediately after a laser pulse corresponds to the formation of the benzyl radical during the decomposition of the starting ketone (reaction (2)). The subsequent increase in the signal indicates the formation of benzyl radicals in decarbonylation of phenylacetyl radicals (reaction (3)). The slow decrease in the signal corresponds to the bimolecular decay of the radicals (reactions (4)—(6)), which is well observed in a longer time scale.

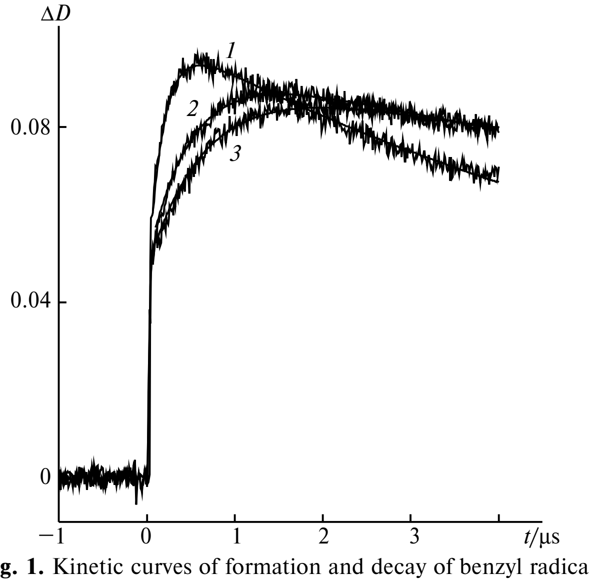


Fig. 1. Kinetic curves of formation and decay of benzyl radicals (314 nm) in hexane (*1*), methanol (*2*), and acetonitrile (*3*) at room temperature. Calculated values (solid lines) are obtained from Eq. (9).

As can be seen in Fig. 1, at room temperature decarbonylation occurs most rapidly in hexane (nonpolar solvent) and most slowly in acetonitrile.

The decarbonylation rate constants k_{CO} at different temperatures were determined in the following way. For every given temperature the kinetics of changing the absorption of benzyl radicals was detected at four different energies of laser pulses in an interval of 1—10 mJ. The initial concentrations of radicals were changed from $2 \cdot 10^{-6}$ to $2 \cdot 10^{-5}$ mol L^{-1}, respectively. The obtained experimental kinetic curves were treated according to Eq. (9). The extinction coefficient of the benzyl radical 6500 mol^{-1} L cm^{-1} was taken from the literature.[10] The rate constants k_{CO} and k_t and initial concentrations of radicals R_0 are variable parameters. As a rule, scatter of the calculated rate constants inside each series did not exceed 5—7%. The calculation is exemplified in Fig. 1.

The temperature dependences of measured rate constants of decarbonylation of the phenylacetyl radical k_{CO} for three solvents are presented in Fig. 2. The data fall on a straight line fairly well and that makes it possible to determine the activation energy of decarbonylation (E_{a}) and pre-exponential factor (A) in the Arrhenius equation. The activation energies and pre-exponential factors are presented in Table 1 along with the k_{CO} values at ∼20 °C, which are in good agreement with the published data.[3,4,10]

According to the classical transition state theory, the influence of the medium on the reaction rate constant can be considered as the difference of the solvation energies for the initial reactants and transition state.

The results obtained can simply be explained qualitatively: since the nonpolar benzyl radical is formed from the polar phenylacetyl radical upon decarbonylation, the transition state is less polar than the initial radical.

The dielectric constant (ε) is used as a measure of solvent polarity in simplest models. The

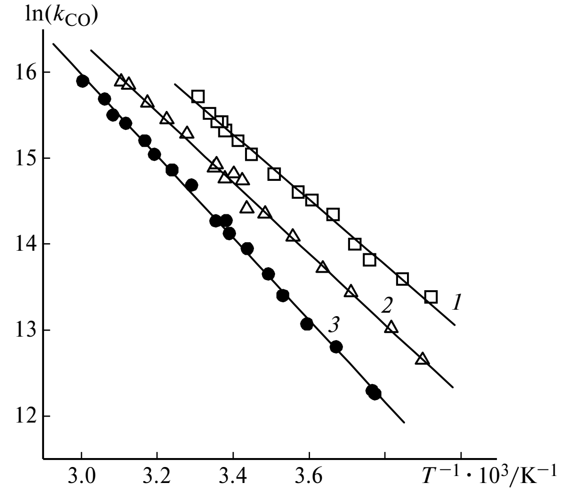


Fig. 2. Arrhenius plots for the rate constant of carbonylation of phenylacetyl radicals in hexane (*1*), isopropyl alcohol (*2*), and acetonitrile (*3*).

Table 1. Rate constants for decarbonylation of phenylacetyl radicals at ~20 °C and parameters of the Arrhenius equation (log (*A*), E_a) for this reaction in various solvents

Solvent	$\frac{\varepsilon-1}{2\varepsilon+1}$	$E_T{}^N$ (Ref. 1)	$k_{CO}\cdot 10^6$ (295 K) / s^{-1}	log(*A*) / s^{-1}	E_a /kJ mol^{-1}
Hexane	0.188	0.009	(4.5±0.3)	12.2±0.3	31.5±0.5
Acetic acid	0.388	0.648	(2±0.2)	11.7±0.3	30.5±0.6
Isopropyl alcohol	0.460	0.546	(2.6±0.2)	12.5±0.3	34.2±0.7
Ethanol	0.470	0.654	(2.4±0.2)	11.5±0.2	28.9±0.4
Methanol	0.477	0.762	(2.2±0.2)	12.1±0.3	32.2±0.6
Acetonitrile	0.480	0.460	(1.4±0.1)	13.1±0.4	39.6±0.7

Kirkwood formula[1] is used to relate the solvation energy to ε

$$\ln(k)-\ln(k_0)=$$

$$=-\frac{\Delta G^{\#}_{\mathrm{solv}}}{RT}=-\frac{1}{4\pi\varepsilon_0}\frac{N_A}{RT}\frac{\varepsilon-1}{2\varepsilon+1}\left(\frac{\mu_a^2}{r_a^3}-\frac{\mu_{\#}^2}{r_{\#}^3}\right),\qquad(10)$$

where k and k_0 are the rate constants in the gas phase and in a hypothetical solvent with ε = 1, $\Delta G^{\#}{}_{\mathrm{solv}}$ is the free solvation energy, N_A is Avogardo's number, and μ_a, $\mu_{\#}$, r_a, and $r_{\#}$ are the dipole moments and radii of the initial radical and transition state, respectively. Model (10) is very simplified and considers a spherical molecule with the point dipole moment in the center, ignoring the real shape, charge distribution, and specific interactions of the dissolved molecule with solvent molecules, for example, the ability of the solvent to form hydrogen bonds. As follows from data in Table 1, the Kirkwood formula is poorly applicable to the description of the solvent effect on the decarbonylation rate constant: despite the Kirkwood parameters $(\varepsilon-1)/(2\varepsilon+1)$ for the reactions in acetonitrile and alcohols are very close, the activation energies for the reactions in these solvents differ noticeably.

A more universal approach is based on the use of the empirical parameters that characterize the solvation capability of the solvent. Among these parameters, the Dimroth E_T scale[1] is most popular. The empirical parameters take into account both the electrostatic and specific interactions between the solvent and solvate. In fact, a good linear correlation between the $E_T(30)$ parameter and logarithm of the reaction rate constant was observed for several reactions, in particular, for the β-scission of alkoxyl radicals.[7,8]

The plot of the activation energy of decarbonylation of phenylacetyl radicals *vs.* $E_T{}^N$ parameter is shown in Fig. 3. It is seen that an attempt to describe the influence of the medium using this parameter gives worse results than the application of the Kirkwood formula. The $E_T{}^N$ parameter is proportional to the energy of electron transition of a standard compound in various solvents.[1] An increase in the polarity of the solvent and formation of hydrogen bonds increase this parameter. Therefore, a linear correlation between the $E_T{}^N$ and E_a parameters of the specific reaction is observed only when the electrostatic interactions and formation of hydrogen bonds have the same effect on the rate constant. Assume that the initial radical is more polar than the transition state, whereas the formation of hydrogen bonds stabilizes the transition state more strongly than the initial radical does. In this case, the specific and nonspecific solvations can mutually be compensated. This is precisely the effect which is observed for the decarbonylation of phenylacetyl radicals.

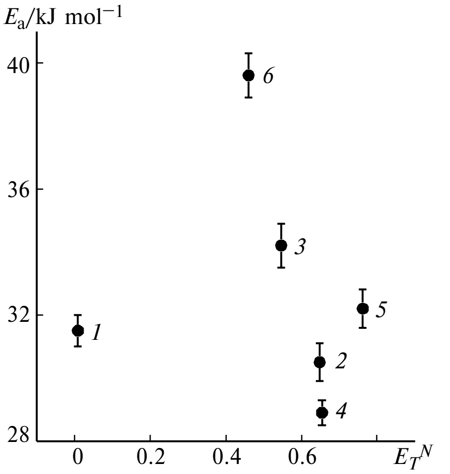
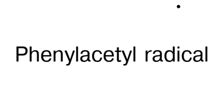


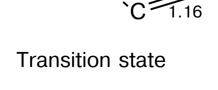
Fig. 3. The plots of the activation energy (E_a) of decarbonylation of phenylacetyl radicals *vs.* $E_T{}^N$ parameter. Solvents: hexane (*1*), acetic acid (*2*), isopropanol alcohol (*3*), ethanol (*4*), methanol (*5*), and acetonitrile (*6*).

To check the assumption on the mutual compensation of two contributions to the difference of free activation energies of decarbonylation, we performed quantum-chemical calculations of nonspecific solvation of the radical and TS and heat of formation of complexes of the radical with alcohol molecules.

Below we present the C—C and C=O bond lengths and spin densities on the C and O atoms in the phenylacetyl radical and in TS of decarbonylation along with spin density distribution calculated by the B3LYP/6-31G* method.



Phenylacetyl radical



Transition state

It is seen that an essential (0.5 Å) elongation of the R—CO bond cleaved in the reaction occurs in TS. The other bond lengths change insignificantly. In addition, the spin density is substantially redistributed from the C atom of the carbonyl group to the C atom of the methylene group. The difference in the electron energies of the TS and initial radical amounts to 37.9 kJ mol^{-1}. Taking into account the difference in energies of zero vibrations, it is equal to 29.9 kJ mol^{-1}, and the difference in enthalpies is 30.4 kJ mol^{-1}, which agrees well with the activation energy measured by us in the nonpolar solvent hexane (31.5±0.5 kJ mol^{-1}).

The electron density redistribution changes the dipole moment from $\mu_a = 7.7 \cdot 10^{-30}$ C m in the radical to $\mu_\# = 5.3 \cdot 10^{-30}$ C m^{-1} in the TS. The PM3 calculations demonstrate a noticeable decrease in the dipole moment of the TS of decarbonylation. Therefore, taking into account only electrostatic interactions with the solvent, an increase in the activation energy with increasing solvent polarity can be expected. The effect of solvent on the difference between free solvation energies of the reactions in hexane $\Delta G^\#_{\text{hex}}$ and acetonitrile $\Delta G^\#_{\text{ACN}}$ was estimated by formula (10). The radius of the initial radical estimated from the molar volume of phenylacetaldehyde similar in size was accepted as $r_a = 3.20$ Å, and that of the transition complex, taking into account the elongation of the R—CO bond, was taken as $r_\# = 3.40$ Å. The obtained value of the difference $\Delta G^\#_{\text{ACN}} - \Delta G^\#_{\text{hex}} = 1.6$ kJ mol^{-1} is much lower than the experimentally determined difference in activation energies of the decarbonylation rate constants in hexane and acetonitrile (see Table 1). This is due to the imperfection of the model of point dipole in the spherical cavity.

Unlike estimations by formula (10), the PCM model (Polarized Continuum Model) takes into account a more realistic shape of the cavity in the solvent and the real charge distribution in the radical. The calculations by this model give the difference in free solvation energies of the transition state and initial phenylacetyl radical in acetonitrile and hexane as $\Delta G^\#_{\text{ACN}} - \Delta G^\#_{\text{hex}} = 4.2$ kJ mol^{-1}, which agrees well with the experimental data.

The difference in enthalpies of formation of complexes of the initial radical and TS with a solvent molecule can be accepted as a measure that characterizes the influence of formation of hydrogen bonds with the solvent on the reaction rate constant. The PM3 calculations for the reaction in methanol show that the heat of formation of a complex with the radical (7.2 kJ mol^{-1}) is much lower than that of a complex with the TS (12.9 kJ mol^{-1}). Therefore, unlike specific solvation, the formation of hydrogen bonds increases the decarbonylation rate constant. The calculated effects of electrostatic interactions with the solvent and formation of hydrogen bonds are close in value and unlike in sign. Thus, the quantum-chemical calculations confirm our hypothesis about the mutual compensation of the contributions of specific and nonspecific solvation to the free activation energy of decarbonylation in alcohols.

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