

Influence of Polar Medium on the Barrier Energy of 1—2 Isomerization of Methoxyl Radical

A Study by *ab initio* Cavity Model

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Using *ab initio* cavitation continuum model on 6-31G** SCF level it was found that polar environment decreases the height of barrier for isomerization of CH₃O radical to CH₂OH radical approximately by 5 kJ mol⁻¹. This rather small energetic effect is predominantly due to the change in quadrupole moment which is higher for the product (CH₂OH radical) than for the transition state. But the barrier is still high enough (about 133 kJ mol⁻¹) to make CH₃O radical kinetically stable.

Oxyl radicals play very often an important role as intermediates at light-initiated oxidation of hydrocarbons or hydrocarbon polymers [1]. *Ab initio* quantum-chemical calculations might be instructive to study both the mechanism and polar medium influence on possible isomerization especially of small oxyl radicals. Methoxyl radical can be intermolecularly converted to the corresponding hydroxymethyl radical which is by 37 kJ mol⁻¹ more stable than methoxyl radical, as shown by the recently published precise quantum-chemical study [2]. The 1—2 isomerization accompanied by hydrogen atom transfer is expected to have a relatively high value of the activation barrier [3]. The paper [4] supplies the value of 109 kJ mol⁻¹. Yet, using high quality *ab initio* calculations in GAUSSIAN-2 (G-2) approximation [5], Pople *et al.* [2] showed that the barrier is significantly higher and its energy equals 138 kJ mol⁻¹. Thus, at room temperature, the intermolecular 1—2 hydrogen rearrangement is hardly possible and the methoxyl radical is kinetically stable, though by ca. 37 kJ mol⁻¹ [2] less stable than the corresponding hydroxymethyl radical. So, the oxyl radical that is formed, for example, at photolytic decomposition of alkyl hydroperoxides (*e.g.* in oxidized hydrocarbon polymers), cannot be rearranged into the corresponding hydroxy radical. Its future depends either on reaction of β -decay (with subsequent scission of the main hydrocarbon chain) or on abstraction of hydrogen from other molecule, resp. on reaction with an oxygen molecule forming the hydroperoxyl radical and a corresponding ketone.

This work deals with the theoretical calculation of the influence of polar environment using *ab initio* cavity model [6], on energetics of 1—2 isomerization of a methoxyl radical. It is well-known that many radical reactions take place in polar environments. For

instance, at photooxidation of hydrocarbon polymers we can observe formation of nonhomogeneous regions, the so-called oxidized polymer domains where predominantly radical oxidation and degradation reactions occur. The value of relative permittivity of such domains can range roughly from 5 to 10. Elaborated theoretical cavitation model [6, 7] is semi-quantitatively very suitable for the description of the influence of polarity of environment on energetic changes. Moreover, in case of the mentioned isomerization reaction the cavitation model is especially suitable since the size of the cavity does not change too much during transition of the reactant to the product. It means that cavitation energy as well as dispersion energy is assumed to be constant.

METHOD

Calculation for the system in vacuum as well as the system in polarizable environment was carried out by the modified version of MONSTERGAUSS program [8]. Since we are talking about the open-shell system, the UHF method has been used.

The applied model for including the influence of the environment can be briefly summarized by the following steps:

i) A solute molecule is placed in a cavity created from interpenetrating spheres centered on its atomic nuclei. The radii values for respective atoms were taken from the papers of the authors of the method [6—8] (C: 1.92×10^{-10} m, O: 1.68×10^{-10} m, and H: 1.44×10^{-10} m). These values represent the corresponding van der Waals radii, increased by 20 %.

ii) Polarization of dielectricum by the presence of solute molecule is approximated by the set of point charges, localized on the cavity surface.

iii) These point charges are incorporated into Fock operator of solute molecule and corresponding HF equations are solved by the standard *ab initio* SCF method.

iv) Steps (ii) and (iii) are repeated until the required degree of self-consistency is reached.

RESULTS AND DISCUSSION

Tables 1 and 2 show the results of calculations. The calculations were carried out in the 6-31G** basis. On the SCF energetic hypersurface, the minima for reactant ($\text{CH}_3\text{O}^\bullet$) and product ($\dot{\text{C}}\text{H}_2\text{—OH}$) have been found and corresponding transition state of C_s symmetry was identified with the help of vibration analysis as TS of the first order with one imaginary frequency. These SCF calculations for vacuum

Table 1. HF/6-31G** Energies of Reactant, TS, and Product ($-E/E_h$)

Species	Symmetry	Vacuum	Solvent ($\epsilon_r = 78.5$)
CH_3O	C_s	114.42558	114.43163
H_2COH	C_1	114.41912	114.42696
$\text{H}_2\text{C(H)O}$ (TS)	C_s	114.34032	114.34828

Table 2. HF/6-31G** Calculated Values of Electrostatic Part of Helmholtz Free Energy of Solvation (ΔF) and Dipole Moments

Species	Symmetry	ΔF	Dipole moment
		kJ mol^{-1}	10^{-30} Cm
CH_3O	C_s	-15.9	8.13
H_2COH	C_1	-20.5	6.43
$\text{H}_2\text{C(H)O}$ (TS)	C_s	-20.9	8.82

indicate that the product radical $\text{H}_2\dot{\text{C}}\text{—OH}$ is by 17 kJ mol^{-1} less stable than the original radical $\text{CH}_3\text{O}^\bullet$ and activation energy of the studied isomerization reaction is $223.8 \text{ kJ mol}^{-1}$. These results show that the inclusion of electron correlation is an effect of qualitative importance; it decreases the energy of CH_2OH radical relatively to CH_3O roughly by 54 kJ mol^{-1} so making the former more stable. This effect is mainly due to the interpair correlation between CH fragments. The G-2 method already includes the electron correlation and decreases the energetic barrier to $138.1 \text{ kJ mol}^{-1}$ [2]. The decrease of the barrier of radical reactions due to an inclusion of the correlation energy is quite a general feature. The G-2 method, as opposed to the SCF method, prefers $\text{H}_2\dot{\text{C}}\text{—OH}$ radical with respect to CH_3O radical by 36.8 kJ mol^{-1} [2]. One must say that

* Calculated components of quadrupole moment tensor relative to the centre of mass are (in 10^{-40} Cm^2) for $\text{CH}_2(\text{H})\text{O}$: -5.844, 0.3539, 5.490 and for H_2COH : -10.588, -4.868, 15.456.

TS on the SCF level has much more extensive spin contamination ($\langle S^2 \rangle = 0.7965$) than both the reactant ($\langle S^2 \rangle = 0.7575$) and the product ($\langle S^2 \rangle = 0.7591$). Thus spin pure SCF wavefunction of TS should have lower energy [9, 10]. It is interesting to note that the transition structure is of higher symmetry (C_s) than that of the product $\text{H}_2\dot{\text{C}}\text{—OH}$ (C_1). This radical is not planar with the CH_2 group slightly pyramidal.

Considering the effect of polar environment expressed through electrostatic part of solvation energy (Table 2), this prefers $\text{H}_2\dot{\text{C}}\text{—OH}$ radical by 4.6 kJ mol^{-1} and also decreases the barrier of isomerization by 5 kJ mol^{-1} . This effect is caused mainly by considerably larger quadrupole moment in $\text{H}_2\dot{\text{C}}\text{—OH}$ radical compared to TS.* Evidently the solvation energy difference is not predominantly due to a change of dipole moment (see Table 2). Since the effect of electron correlation on the overall charge distribution of solute molecule is practically negligible, calculations of electrostatic part of solvation energy using the SCF charge distribution are sufficient. Thus, the used theoretical level (HF/6-31**//HF/6-31**) is not suitable for the quantitative determination of energetic hypersurface of the examined reaction, yet, the conclusions about the influence of environment in cavitation model are sufficient on this SCF level and can be combined with the results of methods of much higher quality (e.g. G-2) used for molecules *in vacuo*.

The above results indicate that the electrostatic part of solvation energy decreases the barrier of 1–2 hydrogen migration in $\text{CH}_3\text{O}^\bullet$ radical approximately by 5 kJ mol^{-1} , which is rather a small effect. Thus, the barrier in the polar environment is still high (about 133 kJ mol^{-1}), making the radical kinetically very stable.

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