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Reactivity of Alkoxy Radicals in β-Cleavage Reactions

O. M. Zarechnaya, I. A. Opeida, and A. F. Dmitruk

Litvineneko Institute of Physical Organic Chemistry, Ukrainian Academy of Sciences, Donetsk, 340114 Ukraine
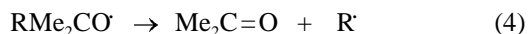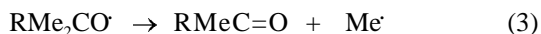
Abstract—The reactivity of alkoxy radicals in β-cleavage reactions depends mostly on the nature of the leaving radical and not on the character of the arising ketone. The reactivity criteria based on isolated molecule approximation provide only qualitative relations. Yet the use of activation parameters calculated by quantum-chemical methods affords good quantitative correlations between the structure and the reactivity of alkoxy radicals in β-cleavage reactions.

Peroxides are extensively used as initiators of radical reactions. The thermal decomposition of peroxides furnishes alkoxy radicals $R_3CO^{\cdot}$ that are predominantly consumed in reactions of β-cleavage and hydrogen abstraction from solvent molecules.

$$R_3CO^{\cdot} \rightarrow R_2C{=}O + R^{\cdot} \tag{1}$$

$$R_3CO^{\cdot} + XH \rightarrow R_3COH + X^{\cdot} \tag{2}$$

The ratio of β-cleavage (1) rate constant (k_f) and hydrogen abstraction (2) rate constant (k_H) from cyclohexane molecule at variation of substituent R structure is known [1] to vary within several orders of magnitude. The ratios of these constants k_f/k_H measured at 313 K are listed in Table 1.

At different R in the alkoxy radical its decomposition can take alternative paths that may be represented for $RMe_2CO^{\cdot}$ as follows:

$$RMe_2CO^{\cdot} \rightarrow RMeC{=}O + Me^{\cdot} \tag{3}$$

$$RMe_2CO^{\cdot} \rightarrow Me_2C{=}O + R^{\cdot} \tag{4}$$

Thus the interpretation of the experimental data on the reactions of alkoxy radicals requires the consideration of two theoretical problems: estimation of the ratio between the rates of the radical β-cleavage and hydrogen abstraction; and the effect of the substituents R in the radical with different structures on the prevalence of one among the possible paths of its decomposition.

The data available up till now permit the following conclusion on the effect of the substituent character on its ability to be eliminated at the β-cleavage of the alkoxy radical: The probability of the elimination grows with the bulk of the substituent [1]. This correlation is actually observed in the radical series $RMe_2CO^{\cdot}$ with substituents R = Me, CH_2Cl, Et, *i*-Pr, *t*-Bu, Ph, $PhCH_2$. We showed by statistical analysis that the correlation factor between the volume of the substituent *v* [2] and $\log(k_f/k_H)$ is small (0.72), and this correlation is only qualitative.

Since the solvation effects are not significant for the reactions of alkoxy radicals [3] their reactivity in the gas phase and in solution is virtually the same. Therefore the reactions with participation of alkoxy radicals are convenient objects for quantum-chemical calculations.

Semiempirical calculations were carried out in AM1 approximation [4] (MOPAC93 software [5]) since this procedure gives the least error in estimation of formation enthalpy of oxygen-containing radicals [6]. The full optimization of the reactants and the reaction products geometry was performed in the approximation of unrestricted Hartree-Fock self-consistent field method (UHF SCF).

Since the prevalence of reaction (3) or (4) will be determined by the stabilization energy of the arising free radical and the strength of the weakest C–C bond a dependence should be expected of the fragmentation ability of the bond on its characteristics, namely, on its length, bond order, and force constant.

The data listed in Table 1 show that in nearly all radicals under consideration the C–R bond is weaker than C–Me bond. The only exception is $PhMe_2CO^{\cdot}$ radical where the C–Ph bond is stronger. The value $\log(k_f/k_H)$ is in slight linear correlation with such characteristics as bond length, bond order, and force constant [in the case of $PhMe_2CO^{\cdot}$ radical the decomposition was regarded as proceeding along reaction (3) corresponding to the cleavage of the weakest bond]. The correlation factors obtained (0.84 for the length of C–C bonds, 0.70 for bond orders, and 0.80 for force constants) indicate that these relations should be regarded as merely qualitative.

Table 1. Bond lengths l(C–Me), l(C–R)Å, force constants K(C–Me), K(C–R) (min/Å), bond orders P(C–Me), P(C–R), P(C–O) in the original radicals RMe_2CO (calculated by AM1 procedure), experimental values of constants ratio k_f/k_H

R	l(C–Me)	l(C–R)	K(C–Me)	K(C–R)	P(C–Me)	P(C–R)	P(C–O)	k_f/k_H
Me	1.531	1.531	1.827	1.827	0.955	0.955	1.078	0.021
CH_2Cl	1.532	1.536	1.762	1.797	0.944	0.952	1.079	0.121
Ph	1.538	1.511	1.693	2.050	0.935	0.948	1.079	0.477
Et	1.535	1.537	1.760	1.759	0.945	0.953	1.078	2.09
i-Pr	1.535	1.546	1.766	1.628	0.945	0.939	1.075	76.4
$PhCH_2$	1.535	1.541	7.766	1.708	0.941	0.943	0.072	250.0
t-Bu	1.537	1.556	1.738	1.478	0.943	0.926	1.075	>300.0

Table 2. Calculated enthalpy ΔH (kJ mol^{-1}) and entropy ΔS (J mol^{-1} K^{-1}) of reactions (2–4), 298 K

R	$-\Delta H(2)$	$\Delta S(2)$	$\Delta H(3)$	$\Delta S(3)$	$\Delta H(4)$	$\Delta S(4)$
Me	96.65	23.43	3.35	170.30	3.35	170.29
CH_2Cl	95.40	13.39	7.95	156.90	−35.98	192.05
Ph	92.05	20.50	−2.51	158.16	35.98	209.62
Et	94.14	20.92	1.26	149.80	−33.47	202.09
i-Pr	93.30	22.18	−2.10	165.70	−113.40	241.00
$PhCH_2$	95.40	19.25	−0.42	156.48	−77.40	216.73
t-Bu	92.05	22.18	−6.70	166.10	−106.30	215.48

The calculated thermodynamic parameters of reactions (2–4) are given in Table 2. The results obtained indicate that the heat evolution and entropy change in reactions (2, 3) are determined mainly by the nature of the eliminated radical and not by the character of the ketone formed. The thermodynamic parameters of reaction (2) are insensitive to the nature of the alkoxy radical.

Note that the enthalpy of reaction (4) is in an approximate correlation with $\log(k_f/k_H)$ (correlation factor 0.90).

Summing up the above stated we can conclude that taking into account only the characteristics of reagents we obtain only qualitative suggestions concerning the effect of radical structure on the kinetic parameters of the reactions under study. Yet it is presumable that the direct calculation of the activation parameters would provide more proper description of reactivity variations depending on the changing structure in the radical series under study.

To this end we carried out quantum-chemical calculations of reaction paths and the corresponding thermodynamic and activation parameters of reactions (2–4) occurring with alkoxy radicals listed above.

The localization of the transition states (TS) for reactions (2–4) was performed in AM1 approximation by unrestricted Hartree–Fock method. The starting geometry of the saddle point for reaction (2) was obtained by procedure from [7]. The saddle points on the potential energy surface corresponding to TS were localized by Bartel method. The found saddle points were tested by two procedures. Firstly, a numerical harmonic vibrational analysis was carried out by calculation of a weighted average Hessian, the frequencies and forms of normal vibrations were obtained; one among them was imaginary and corresponded to a mode of C–C bond vibration for reactions (3, 4) and to the mode of antisymmetrical vibration of C–H–O atoms of the reaction center in the case of reaction (2). Secondly, with the use of IRC method the internal reaction coordinate was constructed in the weighted average Cartesian coordinates (Figs. 1, 2). The initial perturbation was taken equal to a quantum of vibration energy in the direction of the normal coordinate, and also reversible perturbation in the counter direction to the normal coordinate. Thus the internal reaction coordinate was built up starting with TS and descended along the reaction channels both in directions of reactants and reaction products. It is seen from Figs. 1, 2 that TS actually

connect the reactants and the reaction products. The decrease in potential energy on the route from TS is monotone in both directions.

The values of imaginary frequencies $\nu^{\neq}$ (Table 3) evidence that for reactions (3) and (4) the curvature of the potential energy surface in the vicinity of TS is approximately equal, and same as with reaction (2) it weakly depends on the character of the reactants. In the TS of reactions (3, 4) the elongation of the C–C bond to be ruptured compared with the original length is more sensitive to the character of the leaving radical than to the nature of the forming ketone. The geometrical parameters of the reaction center in reaction (20 (elongation of the cleaving bond C–C and the forming bond O–H) are virtually independent of the nature of the alkoxy radical.

The calculated bond orders show that in the TS as compared with the original state the bond order of C–C decreases from 0.93 to 0.41, and the C=O bond order increases on the average from 1.07 to 1.50. The variation of bond orders as a function of structure in the series of the radicals under study (Table 3) indicates the following relation: the easier the radical is cleaved, the higher is the bond order of C–C within the TS, i.e., at the lower stability of the radical the TS is closer in the structure to the original alkoxy radical.
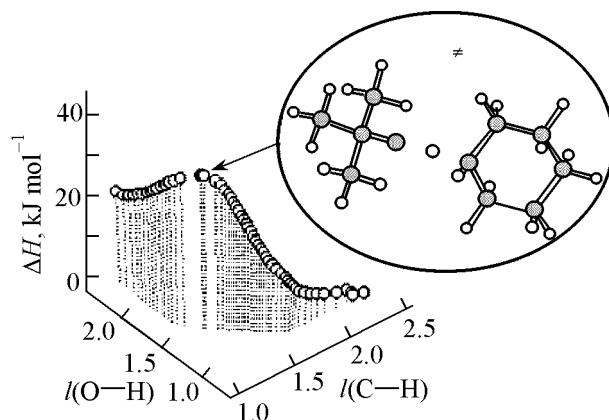

Fig. 1. Reaction path for $t\text{-BuO}^{\cdot} + cyclo\text{-}C_6H_{12} \rightarrow t\text{-BuOH} + cyclo\text{-}C_6H_{11}^{\cdot}$.

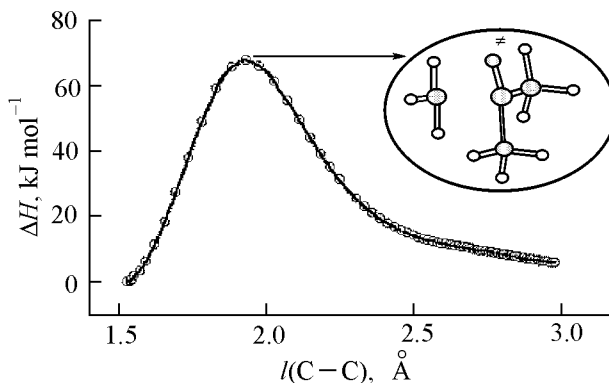**Fig. 2.** Reaction profile for $t\text{-BuO}^{\cdot} \rightarrow Me_2C{=}O + CH_3^{\cdot}$.

Table 3. Geometrical parameters of reaction centers $\Delta l^{\neq}$ (Å), bond orders $P^{\neq}(C\text{–}C)$, $P^{\neq}(C\text{–}O)$ and imaginary frequencies values $\nu^{\neq}$ (cm^{-1}) in transition states of reactions (2–4)

R	Reaction (2)			Reaction (3)				Reaction (4)			
	$\Delta l^{\neq}(C\text{–}H)$	$\Delta l^{\neq}(O\text{–}H)$	$-\nu^{\neq}$	$\Delta l^{\neq}(C\text{–}C)$	$P^{\neq}(C\text{–}C)$	$P^{\neq}(C\text{–}O)$	$-\nu^{\neq}$	$\Delta l^{\neq}(C\text{–}C)$	$P^{\neq}(C\text{–}C)$	$P^{\neq}(C\text{–}O)$	$-\nu^{\neq}$
Me	0.11	0.39	2046	0.40	0.413	1.518	860	0.40	0.413	1.518	860
CH$_2$Cl	0.11	0.40	1952	0.36	0.454	1.462	892	0.41	0.405	1.530	826
Ph	0.11	0.40	1966	0.43	0.351	1.546	766	0.40	0.412	1.494	799
Et	0.11	0.39	2038	0.37	0.456	1.461	812	0.40	0.412	1.517	822
i-Pr	0.11	0.39	2046	0.35	0.484	1.423	803	0.40	0.417	1.511	816
PhCH$_2$	0.11	0.39	985	0.33	0.488	1.418	886	0.40	0.408	1.510	805
t-Bu	0.11	0.39	2067	0.33	0.511	1.387	837	0.40	0.419	1.501	798

Table 4. Calculated enthalpy $\Delta H^{\neq}$ (kJ/mol) and entropy $\Delta S^{\neq}$ (J mol^{-1} K^{-1}) of activation for reactions (2–4)

R	$\Delta H^{\neq}(2)$	$-\Delta S^{\neq}(2)$	$\Delta H^{\neq}(3)$	$\Delta S^{\neq}(3)$	$\Delta H^{\neq}(4)$	$\Delta S^{\neq}(4)$
Me	60.17	192.2	67.53	7.70	67.53	7.70
CH$_2$Cl	61.42	213.3	69.33	2.89	60.30	0.42
Ph	64.10	209.5	63.18	0.84	97.07	3.01
Et	61.88	208.4	63.18	6.11	57.32	5.82
i-Pr	62.17	209.2	63.18	4.98	46.44	-7.15
PhCH$_2$	61.21	235.4	63.41	-1.34	41.76	-15.15
t-Bu	62.76	210.5	65.56	2.30	38.83	16.74

Activation parameters of the reactions studied are presented in Table 4. For reactions (3, 4) the Gibbs free energy is governed mainly by the enthalpy factor, for reaction (2) the entropy term also gives a significant contribution. The results obtained evidence that the β-cleavage along reaction (4) occurs with lower activation enthalpy than in reaction (3) save the $PhMe_2CO^{\cdot}$ radical where the leaving radical is not phenyl but methyl which is a σ-radical.

The data of Table 4 were used in calculation of relative activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$) of the chemical transformations of alkoxy radicals

$$\Delta H^{\neq} = \Delta H^{\neq}(4) - \Delta H^{\neq}(2)$$
$$\Delta S^{\neq} = \Delta S^{\neq}(4) - \Delta S^{\neq}(2)$$

In the case of $PhMe_2CO^{\cdot}$ radical instead of $\Delta H^{\neq}(4)$ and $\Delta S^{\neq}(4)$ values were used the activation parameters of reaction (3). The following correlation equation was obtained for the relative activation parameters and the values of logarithm of the ratio between rate constants of decomposition and hydrogen abstraction:

$$\log(k_f/k_H) = -(0.144 \pm 0.011)\Delta H^{\neq} - (0.003 \pm 0.000)\Delta S^{\neq}$$
$$r\ 0.97,\ s\ 0.32.$$

It should be noted that the coefficient for $\Delta H^{\neq}$ is close to the value ($1/RT$); thus the equation obtained is very similar to analytical one.

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