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SHORT COMMUNICATIONS

Investigation of the Molecular Dynamics of Some Phenols and Their Acetyl Isomers in Solutions by NMR Relaxation

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Abstract—The dynamics of relaxations and Fries rearrangements in phenol acetates and their acetyl isomers was studied by the NMR relaxation technique in acetone-d_6. The results of ^{13}C and ^{1}H spin-lattice nuclear relaxation measurements show that these experiments can be used for determining the mobility and activation energies of the molecular motions of compounds in different systems.

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INTRODUCTION

Recent achievements in nuclear magnetic studies are of great theoretical and practical value. In particular, nuclear relaxation (theory and applications) was discussed in numerous publications, the number of which is constantly growing.

Nuclear magnetic relaxation spectroscopy is a convenient tool for comparing the theoretical models of molecular structure and investigating the relaxation mechanisms in studies of the dynamics of various solutions; it can also be used for determining the activation energies of molecular motions, intra- and intermolecular interactions, complexations, associations, etc. [1–12].

As is known, carbonyl-substituted alkenylphenols are used as reagents in organic synthesis and stabilizer monomers in polymerizations [13]. It is therefore interesting to study various acetate- and acetyl-substituted phenols by NMR relaxation spectroscopy and to reveal a relationship between their structure and behavior in the systems under study.

EXPERIMENTAL

The samples were studied on an Avance 300 Bruker pulse spectrometer at an operating frequency of 300 MHz for ^{1}H and 75 MHz for ^{13}C (TopSpin 3.1 software) equipped with a BVT 3200 temperature sensor. The error of the sensor was not more than ±1 K.

The spin-lattice relaxation was evaluated by the standard procedure using an inversion–reduction pulse sequence [T-180-τ-90°] (the measurement error was ±0.01–0.10 s).

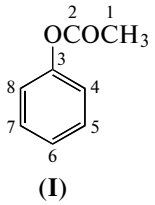
The activation parameters of molecular motions were calculated by the equation [3]

$$E = 19.13[T^{(1)}T^{(2)}/(T^{(2)} - T^{(1)})]\log(T_1^{(2)}/T_1^{(1)}),$$

where $T^{(1)}$ and $T^{(2)}$ are the temperatures corresponding to the relaxation times $T_1^{(1)}$ and $T_1^{(2)}$. The calculation error was ±0.1–0.5 kJ/mol. The NOE factor was calculated from the intensity ratio in the spectra recorded with full suppression of spin–spin proton coupling and decoupling only during spectrum measurements [14]. The samples were studied in acetone-d_6 and CCl_4 solutions (a few drops of acetone-d_6 were used for a lock signal for CCl_4 solutions). The Fries rearrangements of phenol esters were performed in the presence of $AlCl_3$ or under UV irradiation by known procedures [15–17].

RESULTS AND DISCUSSION

As model compounds, we used phenylacetate **I**, *p*-tolyl acetate **III**, and their derivatives 2-hydroxyacetophenone **II** and 2-hydroxy-5-methylacetophenone **IV** obtained by the Fries rearrangement



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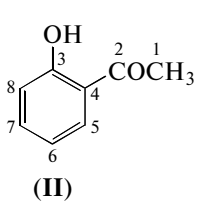

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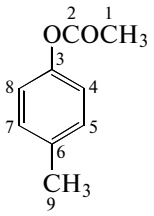

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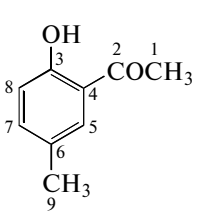


(IV)

Table 1. ^{1}H and ^{13}C spin-lattice nuclear relaxation times (T_1) and activation energies of the molecular motion in 5 and 10% acetone-d_6 solutions at different temperatures (x is the concentration of a compound)

x, %	Fragment	−20°C	−5°C	5°C	22°C	40°C	50°C	E, kJ/mol
				I				
5	$COCH_3$ (^{1}H)	2.43	3.68	4.51	4.73	5.25	5.81	8.45
10		2.35	3.27	4.45	4.55	5.13	5.75	8.68
5	$COCH_3$ (^{13}C)	–	–	–	12.37	12.60	–	–
10		7.28	8.53	10.27	11.49	11.65	12.04	4.88
				II				
5	$COCH_3$ (^{1}H)	1.94	2.15	2.33	3.27	3.68	3.89	6.75
10		1.85	2.03	2.22	2.98	3.33	3.78	6.93
5	$COCH_3$ (^{13}C)	–	–	–	11.61	11.93	–	–
10		7.23	8.18	10.23	10.48	10.77	11.35	4.37
				III				
5	$COCH_3$ (^{1}H)	2.38	2.91	3.43	3.77	4.61	5.64	8.37
10		2.19	2.69	3.05	3.70	4.52	5.22	8.42
5	$COCH_3$ (^{13}C)	–	–	–	9.29	–	12.31	–
10		5.87	7.47	8.05	9.40	11.43	12.03	6.96
5	$ArCH_3$ (^{1}H)	1.83	2.17	3.38	3.75	4.57	4.74	9.23
10		1.83	2.14	2.97	3.29	4.12	4.68	9.11
5	$ArCH_3$ (^{13}C)	–	–	–	8.58	–	9.55	–
10		5.86	7.28	8.10	9.05	9.19	9.32	4.50
				IV				
5	$COCH_3$ (^{1}H)	1.73	3.06	3.28	4.13	4.33	4.82	9.94
10		1.53	2.79	3.17	4.09	4.10	4.26	9.93
5	$COCH_3$ (^{13}C)	–	–	–	8.69	–	12.03	–
10		5.32	6.28	7.19	8.14	9.76	10.97	7.02
5	$ArCH_3$ (^{1}H)	2.48	3.17	3.75	4.78	5.33	5.46	7.65
10		2.43	3.14	3.55	4.19	5.34	5.41	7.76
5	$ArCH_3$ (^{13}C)	–	–	–	8.63	–	10.21	–
10		8.15	9.07	9.23	9.42	10.71	11.61	3.43

For the methyl groups of all the four compounds, we calculated the ^{1}H and ^{13}C spin-lattice nuclear relaxation times (T_1) at different temperatures and concentrations in deuteroacetone solutions. The dipole–dipole C–H mechanism was found to prevail for these fragments; this is typical of the dipole–dipole mechanism of relaxation at elevated temperatures, with spin-lattice relaxation times increasing concurrently. The activation energies of the molecular motion were determined from the temperature dependence of spin-lattice relaxation that is due to the dipole–dipole mechanism [3, 7] (Table 1). The activation energies of the molecular motion for the methyl groups on ^{1}H and ^{13}C nuclei are different, indicating that anisotropic molecular reorientations occur in the liquid [1].

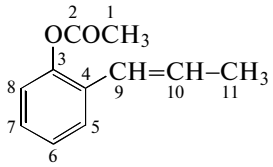
Given below are the structural formulas of 2-propenylphenylacetate **V** and the product of its Fries rearrangement 2-hydroxy-3-propenylacetophenone **VI**:

Table 2. ^{1}H and ^{13}C spin-lattice nuclear relaxation times (T_1) and activation energies of the molecular motion of compounds **V** in 5 and **VI** in 10% acetone-d_6 solutions at different temperatures

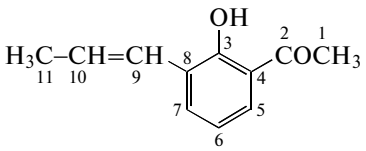
Fragment	22°C	40°C	Fragment	x, %	−20°C	−5°C	5°C	22°C	40°C	50°C	E, kJ/mol
V							**VI**				
$COCH_3$ (^{1}H)	2.99	3.78	$COCH_3$ (^{1}H)	5	–	–	–	2.21	2.97	–	–
$COCH_3$ (^{13}C)	7.29	9.06		10	1.40	1.59	1.96	2.15	2.85	3.76	9.58
CH_3 (^{1}H)	3.62	4.40	$COCH_3$ (^{13}C)	5	–	–	–	8.25	8.98	–	–
CH_3 (^{13}C)	7.07	8.54		10	3.05	4.86	6.93	7.23	8.76	9.45	10.97
CH (^{13}C)	4.15	5.70	CH_3 (^{1}H)	5	–	–	–	3.81	4.71	–	–
CH (^{13}C)	4.06	5.63		10	1.90	2.57	3.32	3.46	4.38	4.53	8.43
CH (^{13}C)	4.09	5.23	CH_3 (^{13}C)	5	–	–	–	8.03	9.72	–	–
CH (^{13}C)	4.01	5.21		10	4.96	5.43	7.37	7.76	9.34	10.83	7.57
=CH (^{13}C)	6.16	7.46									
=CH (^{13}C)	6.16	8.59									

Table 3. Spin-lattice nuclear relaxation times (T_1), η NOE factor, and DD and SR relaxation mechanisms for hydrogen-bearing ^{13}C at 22°C

Atom	η	T_1, s	α, %	R_1^{SR}, s^{-1}	T_1^{SR}, s	α, %	R_1^{DD}, s^{-1}	T_1^{DD}, s
			SR relaxation			DD relaxation		
				I				
C1	1.46	12.37	27	0.0218	45.87	73	0.0590	16.95
C4–C8	1.96							
C5–C7	1.96							
C6	1.88							
				II				
C1	1.51	11.61	24.5	0.0211	47.39	75.5	0.0650	15.38
C5	1.87							
C6	1.92							
C7	1.94							
C8	1.81							
				III				
C1	1.47	9.29	26.5	0.0285	35.09	73.5	0.0791	12.64
C4–C8	1.90							
C5–C7	1.88							
C9	1.27	8.58	36.5	0.0425	23.53	63.5	0.0740	13.51
				IV				
C1	1.56	8.69	22	0.0253	39.53	78	0.0898	11.14
C5	1.88							
C7	1.82							
C8	1.80							
C9	1.13	8.63	43.5	0.0504	19.84	56.5	0.0655	15.27
				V				
C1	1.88	7.29	6	0.0082	121.95	94	0.1289	7.76
C5	1.92	4.15	4	0.0096	104.17	96	0.2315	4.32
C6	1.82	4.06	9	0.0222	45.05	91	0.2241	4.46
C7	1.88	4.09	6	0.0147	68.03	94	0.2298	4.35
C8	1.88	4.01	6	0.0149	67.11	94	0.2344	4.27
C9	1.94	6.16	3	0.0049	204.08	97	0.1575	6.35
C10	1.88	6.16	6	0.0097	103.09	94	0.1526	6.55
C11	1.75	7.07	12.5	0.0177	56.49	87.5	0.1238	8.08
				VI				
C1	1.91	8.25	4.5	0.0055	181.8	95.5	0.1158	8.64
C11	1.79	8.03	10.5	0.0131	76.34	89.5	0.1115	8.97



(V)



(VI)

Our studies showed that the dipole–dipole C–H mechanism prevailed for all hydrogen-bearing carbon atoms. Using the temperature dependence for **VI**, we determined the activation energies of the molecular motion that controlled this relaxation mechanism (Table 2).

According to Table 2, the spin-lattice relaxation times T_1 are close for hydrogen-bearing aromatic carbons in **V**. This can be explained by the absence of the dominant rotation axis for this molecule.

A comparison of the relaxation times of two CH_3 groups and CH groups in **V** showed that for CH_3 carbons, T_1 exceeded that of CH carbon. On the basis of these data, we can conclude that spin-rotational (SR) relaxation occurs along with dipole–dipole (DD) relaxation for these groups [4]. The calculated fractions of the DD and SR relaxations for the carbon of the carbonyl and propenyl CH_3 groups are 94 : 6 and 87.5 : 12.5%, respectively.

For **VI**, the data obtained in liquid suggest that a relatively anisotropic molecular reorientation takes place.

For several groups in **I**–**VI**, the dipole–dipole and spin-rotational relaxation times were calculated (Table 3). As is known, **II** and **IV** have an intramolecular hydrogen bond. In continuation of this study, we investigated hydrogen bonding in 2-hydroxy-3-propenylacetophenone **VI** in 5% acetone-d_6 and CCl_4 solutions. In the ^{1}H NMR spectrum, the signal of the hydroxyl group lies at 12.74 ppm. As a result of the interaction with deuteroacetone in the 5% acetone-d_6 solution, the signal of the hydroxyl group shifted to 12.93 ppm. These data suggest that intramolecular hydrogen bonding occurs in this compound too.

The hydrogen bond energies were calculated by Schaefer's method [12]. The intramolecular hydrogen bond energy of **II**, **IV**, and **VI** was found to be 8 ± 1 kcal/mol (for **II** and **IV** in $CDCl_3$ solution, the signal of the hydroxyl group was observed at 12.11 and 12.10 ppm, respectively).

A comparison of the intramolecular hydrogen bond energies of **II**, **IV**, and **VI** with those of *ortho*-aminomethylated alkenylphenols [8] showed that the energies of the latter were smaller than those of *ortho*-acetylphenols. For aminomethylated derivatives, the bond energies varied from 5.2 to 6.3 kcal/mol, which agrees well with the data of [6].

According to Table 3, T_1 for acetyl methyl groups decreased after the Fries rearrangement. This decrease in the mobility of methyl groups could be explained by the intramolecular hydrogen bonding.

The copolymers obtained from 2-hydroxy-3-propenylacetophenone **VI** are proof against light and other factors.

The results of our studies on ^{13}C and ^{1}H spin-lattice nuclear relaxation adequately reflect the dynamics of the behavior of molecules in solution and can be effectively used for determining the compositions, mobility, and activation energies of various systems.

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