ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 3, pp. 390–397. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © T.N. Aksamentova, N.N. Chipanina, A.I. Mikhaleva, B.A. Trofimov, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 3, pp. 400–407.

O-Vinylacetoxime as a Hydrogen Bond Acceptor

T. N. Aksamentova, N. N. Chipanina, A. I. Mikhaleva, and B. A. Trofimov

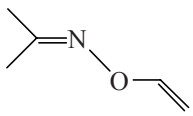
Faworskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033, Russia
e-mail: nina_chipanina@irioch.irk.ru

Received September 1, 2008

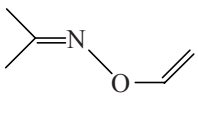
Abstract—According to quantum chemical calculations (B3LYP/6-311G*) and IR spectroscopy the basicity of oxygen atom of *O*-vinylacetoxime is substantially lower than that of *O*-ethylacetoxime and is comparable to the basicity of phenyl vinyl and diphenyl ethers. In CCl_4 solution, *O*-vinylacetoxime gives H-complexes with methanol by formation of N···HO bonds. With phenol and trifluoroacetic acid under these conditions it enters in the reaction of electrophilic addition. *O*-Ethylacetoxime in inert media forms with methanol and phenol two types of H-complexes with the N···HO or O···HO bonds.

DOI: 10.1134/S1070363209030104

O-Vinylketoximes are promising monomers and intermediates, as well as the models for investigation of reactivity of *O*-vinyloxime function. Their chemical modifications makes it possible to purposefully synthesize new compounds with the =N–O system of bonds. *O*-Vinylketoximes are unstable energy-rich compounds (temperature of decomposition 110–150°, energy of decomposition 1300–1800 J g^{-1}) [1]. Their reactivity in electrophilic addition of carboxylic acids and alcohols to the double bond was studied on the example of *O*-vinylbenzophenone oxime [2]. The conformational structure and vibrational spectra of the simplest representative of this class of compounds, *O*-vinylacetoxime **I**, [3–5] and possible intramolecular rearrangements initiated by dissociation of the N-O bond were theoretically studied [6]. It was shown that in the isolated state oxime **I** exists as an equilibrium mixture of two planar conformers: *ap,ap* and *ap,sp*, the former being by 0.62 kcal mol^{-1} (HF/6-311G**) more stable [3–5].



I-*ap,ap*



I-*ap,sp*

The activation parameters and thermal effects of intramolecular rearrangement of this compound into iminoacetaldehyde were estimated and the structure of the transition state was identified [6]. Quantum-chemical study of hydration and protonation of oxime **I** in the gas phase provided a possibility to solve the problem of interrelation between the structure of its stable conformers and their propensity to form H-bonded complexes [7, 8].

In the present work we have studied the interaction of *O*-vinylacetoxime (**I**-*ap,ap*) and (**I**-*ap,sp*) with weak (methanol) and strong (phenol and trifluoroacetic acid) proton donors using the methods of IR spectroscopy and quantum chemistry. When studying the electron-donating ability of oxime **I**, *O*-ethylacetoxime **II** was used as a model compound in which the =N–O fragment is not connected with a highly reactive vinyl group.

Earlier, theoretical study of donor–acceptor interaction of *O*-vinylacetoxime **I** with water and trifluoroacetic acid [7, 9] has shown that its monohydrates are weak H-complexes with the energy of formation ΔE 4–5 kcal mol^{-1} that slightly depends on the conformation of the molecules or the type of the H-bond. All heavy atoms in both conformers of proton-acceptor **I** lie in one plane. Upon the formation of the monohydrate with participation of the oxygen atom, the N–O bond is elongated as compared to the starting molecule. With trifluoroacetic acid strong H-complexes with the N···HO (ΔE 11.1–12.1 kcal mol^{-1}) or O···HO bonds (ΔE 7.8–9.1 kcal mol^{-1} are formed. With this, not only the lengths of the N–O and C–O bonds of oxime **I** but also the mutual orientation of its vinyl and azomethine groups is substantially changed.

We have studied theoretically the H-complexes of the *ap,ap*- and *ap,sp*-conformers of oxime **I** with methanol of 1:1 composition with participation of the nitrogen (**IIIa** and **IIIb**) or the oxygen (**IVa** and **IVb**) respectively, and those of 1:2 composition with participation of both heteroatoms **Va** and **Vb** (see Fig. 1 and Table 1). H-Complexes of **I** with phenol of 1:1 composition with the N···HO (**VI)** and O···HO bond **VII** and of 1:2 composition **VIII** were studied on the example of its more stable conformer **I**-*ap,ap* (see Fig. 2 and Table 1).

By their strength (ΔE 5.4–7.8 kcal mol^{-1}) these H-complexes occupy the intermediate position between the hydrates of oxime **I** and its complexes with trifluoroacetic acid. When the nitrogen atom is involved in their formation, they are more stable by ~2.0 kcal mol^{-1}. H-Complexes of the (**I**-*ap,ap*) conformer with phenol are stronger than those with methanol by only 0.4 (N···HO) or 0.7 kcal mol^{-1} (O···HO).

In all H-complexes of oxime **I** of 1:1 composition the starting conformation of the proton-acceptor is

Table 1. Characteristics of H-complexes of *O*-vinylacetoxime **I**, *O*-ethylacetoxime **II**, vinyl ethyl **XV**, divinyl **XXIV**, diphenyl **XXI**, vinyl phenyl **XXVII**, and diethyl **XVIII** ethers with MeOH and PhOH

Complex	H-acceptor	X···H Bond	B3LYP/6-311G*			IR in CCl_4 solution
			$-\Delta E$, kcal mol^{-1}	d(X···H), Å	$\Delta\nu$(OH), cm^{-1}	$\Delta\nu$(OH), cm^{-1}
			MeOH			
1:1						
IIIa	**I**, *ap,ap*	NH	7.37	2.007	149	154
IIIb	**I**, *ap,sp*	NH	7.78	1.983	172	199
IVa	**I**, *ap,ap*	OH	5.43	2.005	63	
IVb	**I**, *ap,sp*	OH	5.85	2.024	73	
1:2						
Va	**I**, *ap,ap*	OH, NH	12.28	1.949 1.960	54 128	
Vb	**I**, *ap,sp*	OH, NH	12.67	2.030 2.081	63 126	
1:1						
IX	**II**, *ap,ap*	NH	8.32	1.991	182	215
X	**II**, *ap,ap*	OH	7.09	1.949	118	117
1:2						
XI	**II**, *ap,ap*	OH, NH	14.84	1.966 2.007	103 163	
1:1						
XVI	**XV**, *sp,ap*	OH	6.19	1.967	78	
XIX	**XVIII**, *sc,ap*	OH	7.84 [10]		140 [10]	148 [10]
XXII	**XXI**	OH	6.46 [10]		58 [10]	50 [10]
XXV	**XXIV**, *sp,ap*	OH	5.63	2.027	39	
XXVIII	**XXVII**	OH	6.12	2.020	53	

Table 1. (Contd.)

Complex	H-acceptor	X···H Bond	B3LYP/6-311G*			IR in CCl_4 solution
			$-\Delta E$, kcal mol^{-1}	d(X···H), Å	Δν(OH), cm^{-1}	Δν(OH), cm^{-1}
			PhOH			
1:1						
VI	**I**, *ap,ap*	NH	7.82	1.927	260	
VII	**I**, *ap,ap*	OH	6.09	1.953	131	
1:2						
VIII	**I**, *ap,ap*	OH, NH	13.09	2.015 1.962	93 237	
1:1						
XII	**II**, *ap,ap*	NH	9.23	1.913	319	385
XIII	**II**, *ap,ap*	OH	7.28	1.890	208	215
1:2						
XIV	**II**, *ap,ap*	OH, NH	15.48	1.927 1.933	168 282	
1:1						
XVII	**XV**, *sp,ap*	OH	7.15	1.887	152	155 [13]
XX	**XVIII**, *sc,ap*	OH	9.84 [10]		264 [10]	271 [13]
XXIII	**XXI**	OH	6.46 [10]		127 [10]	126 [10]
XXVI	**XXIV**, *sc,ap*	OH	6.08	1.933	111	93 [13]
XXIX	**XXVII**	OH	6.33	1.934	117	107 [13]

retained, variations of dihedral angles C^1=N–O^1–C^2 and N–O^1–C^2=C^3 do not exceed 14º. The lengths of the covalent bonds in the complexes with methanol slightly differ from those in the starting conformers of oxime **I**; the same is true for complexes with phenol with the N···HO bond. At the same time, when the oxygen atom is involved in the complex formation with phenol, the length of both bonds increases by 0.016 (C^2–O^1) and 0.010 Å (N–O^1).

H-Complexes of oxime **I** with methanol **Va, Vb** and phenol **VIII** of 1:2 composition are by 5–7 kcal mol^{-1} more stable than the corresponding 1:1 complexes (Table 1). The molecular conformation of the proton-acceptor in these complexes is also retained. The lengths of the covalent bonds N-O^1 and C^2–O^1 increases by ~0.01 Å with respect to the starting conformers of oxime **I**. As in the complexes of phenol with the O···HO bond, this is indicative of weakening of interaction between the oxygen atom lone pair (LP) and the C=C and N=C groups that determines the stability of the **I**-*ap,ap* and **I**-*ap,sp* conformers.

The interaction of *O*-ethylacetoxime **II** with proton-donors was studied for its *ap,ap*-conformer which is by 0.5 kcal mol^{-1} more stable than the *ap,sp*-conformer (see Fig. 3 and Table 1). H-Complexes of oxime **II** of 1:1 composition with methanol and phenol with the N···HO bonds **IX, XII** are by 1.2 (with methanol) and 1.9 kcal mol^{-1} (with phenol) more stable energetically than those with the O···HO bonds **X, XIII**. With this, they are by 1–2 kcal mol^{-1} more stable than the corresponding H-complexes of oxime **I** having the vinyl group.

Theoretical estimation of the electron-donating ability of oximes **I** and **II** was performed by the use of the Δν(OH) value taken as the difference between the

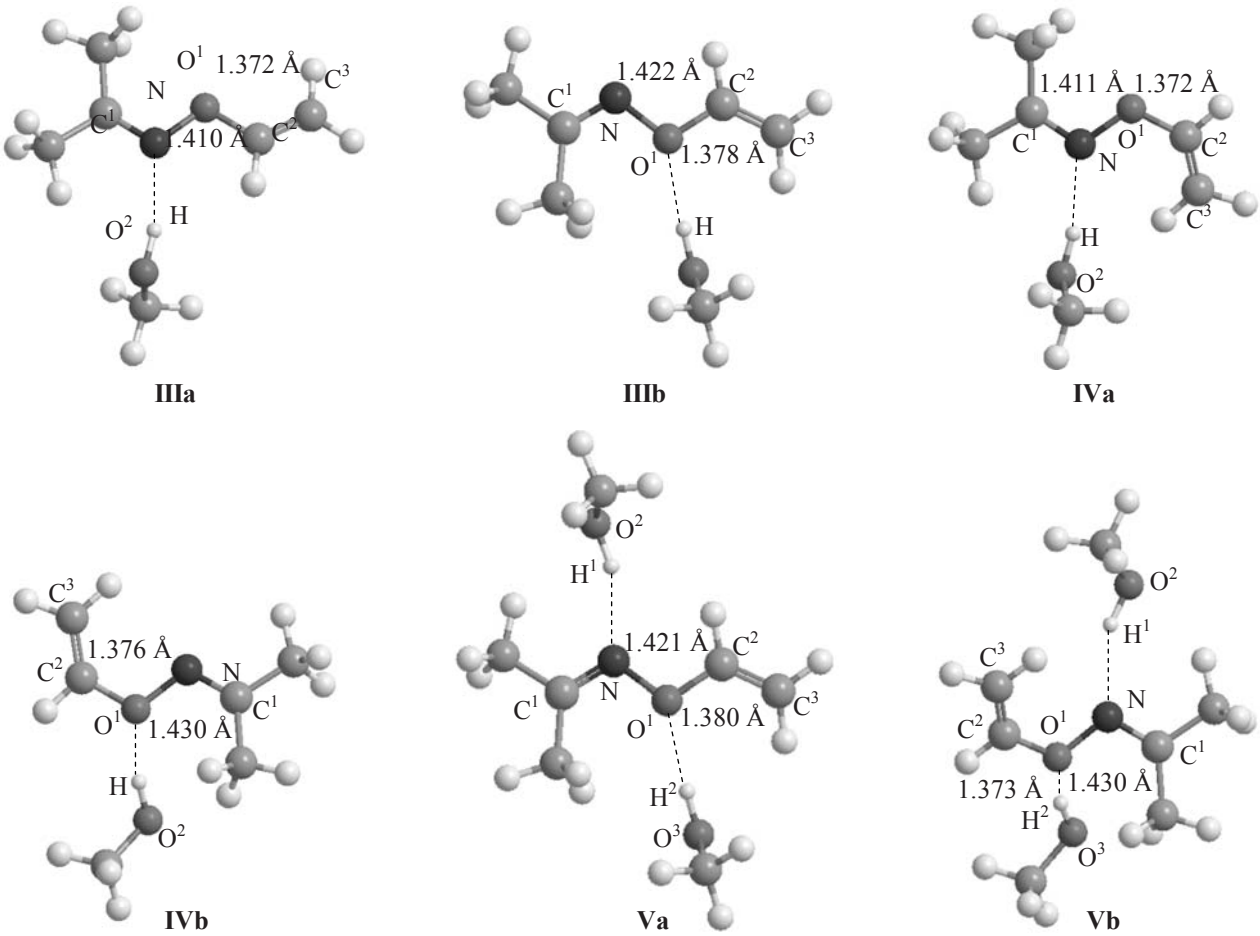


Fig. 1. Molecular structures of H-complexes of *ap,ap*- and *ap,sp*-conformers of *O*-vinylacetoxime **I** with methanol.

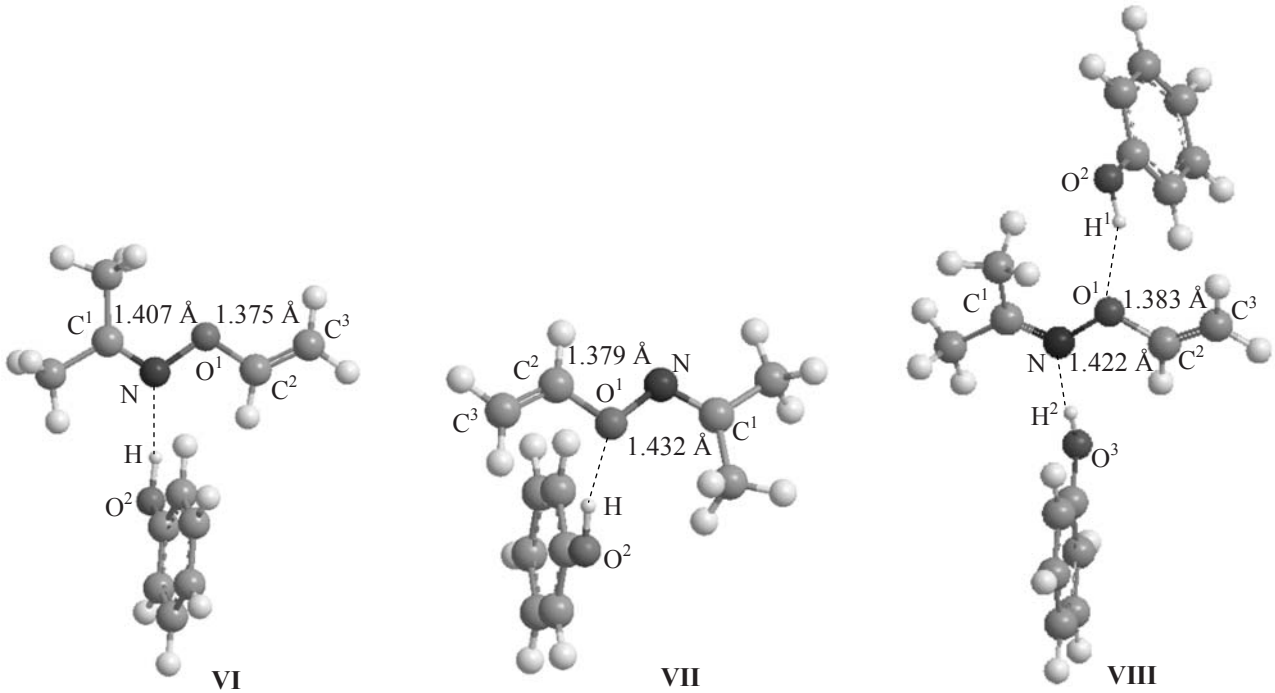


Fig. 2. Molecular structures of H-complexes of *ap,ap*-conformer of *O*-vinylacetoxime **I** with phenol.

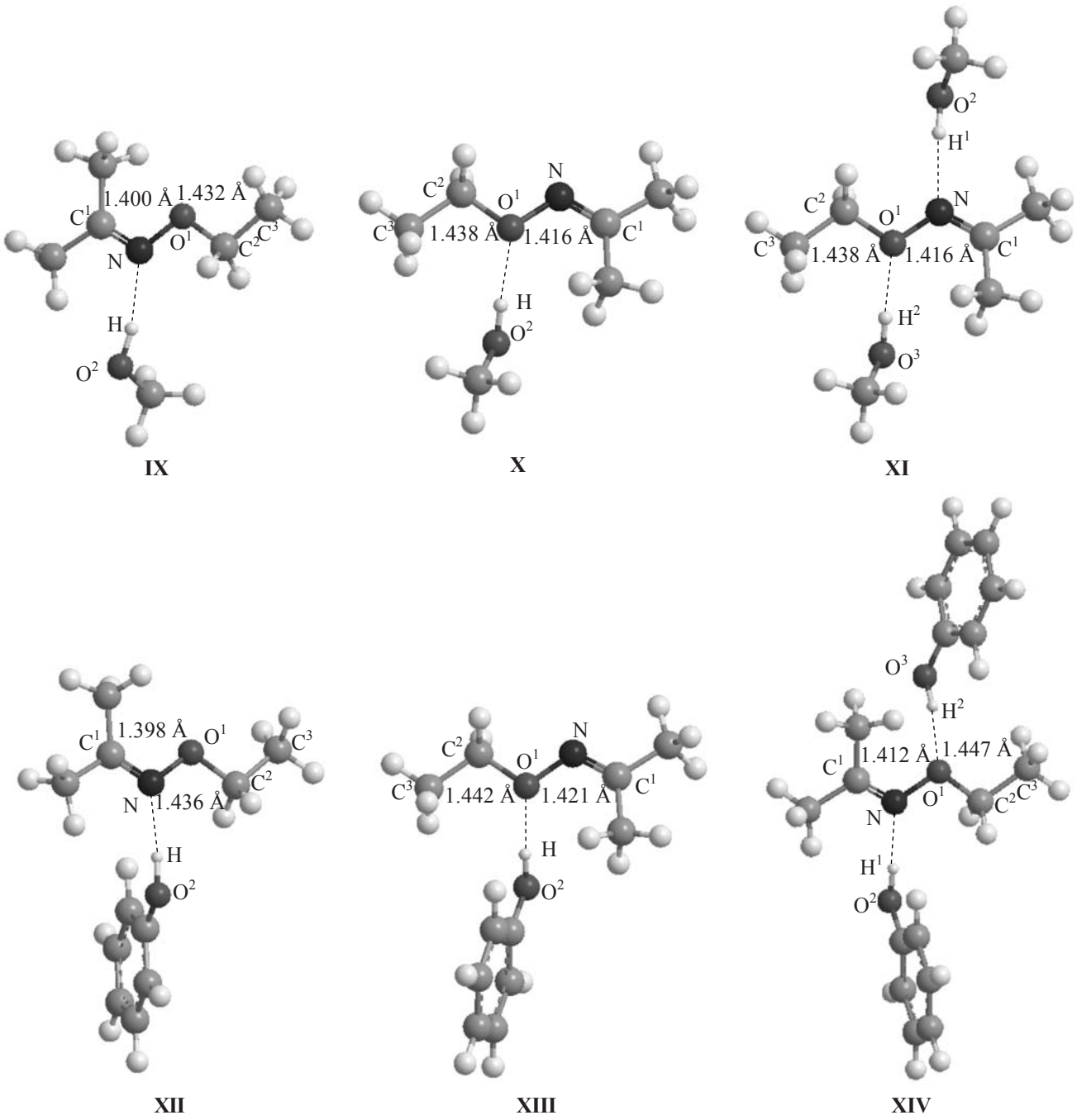


Fig. 3. Molecular structures of H-complexes of *ap,ap*-conformer of *O*-ethylacetoxime **II** with methanol and phenol.

calculated stretching vibration frequencies of the free and associated hydroxy groups of the proton-donor molecule. The values of spectroscopic basicity [Δν(OH)] for H-complexes of methanol with the *ap,ap*- and *ap,sp*-conformers of **I** containing the N···HO bonds amount to 149 (**IIIa**) and 172 cm^{-1} (**IIIb**), and the O···HO bonds, 63 (**IVa**) and 73 cm^{-1} (**IVb**), differing more than twofold (Table 1). This difference is retained also for the similar H-complexes of the *ap,ap*-conformer of oxime **I** with phenol, 260 (N···HO) (**VI**) and 131 cm^{-1} (O···HO) (**VII**). The spectral shift for complexes of oxime **II** as compared to those of oxime **I** increases for the N···HO and O···HO bonds and amounts to 182 (**IX**) and 118 cm^{-1} (**X**) for complexes

with methanol, and 319 (**XII**) and 208 cm^{-1} (**XIII**) for complexes with phenol, respectively (Table 1). According to the data obtained, the basicity of oxygen atom in oxime **I** is 1.9 times less than that in oxime **II**, and the basicity of nitrogen in **I** is 1.2 times less than in **II**. The differences found for the Δν(OH) values makes it possible to determine the electron-donating centers in molecules **I** and **II** upon formation of H-complexes in inert media from the data of IR spectroscopy.

The comparison of the calculated spectral shifts for H-complexes of oximes **I**, **II** and ethers (Table 1) indicated the order of these molecules according to sequences (1) and (2) in keeping with the increasing electron-donating ability of their oxygen atom. The calculations were performed for the most stable conformers of the molecules [11, 12]. Sequence (1) shows the values of Δν(OH) (cm^{-1}) for H-complexes of methanol, sequence (2), for those of phenol. The maximum electron-donating ability is observed in diethyl ether **XVIII**, the minimum, in divinyl ether **XXIV**. The basicity of oxygen atom in oxime **I** is ca. twice as low as that of ether **XVIII**, higher than in divinyl **XXIV** and phenyl vinyl ether **XXVII**, and close to that of diphenyl ether **XXI**.

XXIV (39) < **XXVII** (53) < **XXI** (58)
< **I** (63) < **XV** (78) < **II** (118) < **XVIII** (140), (1)

XXIV (111) < **XXVII** (117) < **XXI** (127)
< **I** (131) < **XV** (152) < **II** (208) < **XVIII** (264). (2)

Since the electron-donating ability of the oxygen atom in unsaturated ethers depends on the character of interaction of its LP with the π-system of the molecules [13], the above order of spectroscopic basicity reflects the degree of this interaction. It is maximum in divinyl ether. In *O*-vinylacetoxime this interaction is comparable with that in diphenyl ether **XXI**. Electron-donating properties of *O*-ethylacetoxime **II** are comparable to those of diethyl ether **XVIII**. This is in compliance with a lower degree of interaction of the oxygen atom LP with the oxime group as compared to the vinyl group [5].

The value of the spectral shift Δν(OH) in the series of the considered H-complexes of oximes and ethers with methanol and phenol linearly depends on the length of hydrogen bond *d*(O···H), Å, determining their strength [Eq. (3)].

$$\Delta\nu(OH) = (1847\pm254) - (888\pm129)d(O\cdots HO), \quad (3)$$
$$r\ 0.92,\ se\ 21,\ n\ 11.$$

Similar linear correlation (4) is observed between the values of spectroscopic basicity of nitrogen atom in the studied oximes and the length of the N···H bond in their H-complexes with methanol and phenol.

$$\Delta\nu(OH) = (3491\pm415) - (1667\pm211)d(N\cdots HO), \quad (4)$$
$$r\ 0.98,\ se\ 18,\ n\ 5.$$

The nature of the interaction of *O*-vinylacetoxime **I** with hydrogen bond donors (methanol, phenol, trifluoroacetic acid) was studied by us using the method of IR spectroscopy in inert media. In the spectrum of solution of *O*-vinylacetoxime **I** in CCl_4 the stretching vibration bands of the C=C groups at 1623, 1648, and the C=N group at 1669 cm^{-1} are observed. A strong band at 1623 cm^{-1} belongs to the (**I**-*ap,ap*)-conformer, and a weak band at 1648 cm^{-1}, to the less stable (**I**-*ap,sp*) conformer [3]. Addition of excess phenol or trifluoroacetic acid to this solution leads to the disappearance of the ν(C=C) vibrations band. At the same time, addition of excess oxime **I** to the diluted solution of phenol or trifluoroacetic acid in CCl_4 (c ~10^{-4}–10^{-5} M) results in disappearance of the OH vibration band of the proton-donor molecule. These changes are indicative of the addition of phenol or trifluoroacetic acid to the C=N bond of oxime **I** with the formation of *O*-(1-phenoxyethyl)- or *O*-(1-trifluoroacetoxyethyl)acetoximes. However, the reaction of addition of trifluoroacetic acid to *O*-vinylbenzophenone oxime with the formation of *O*-(1-trifluoroacetoxyethyl)benzophenone oxime proceeds under more severe conditions (heating of equimolar amounts of the reagents to 60ºC during 0.5 h) [2].

Alcohols are also known to add to *O*-vinylbenzophenone oxime by the Markownikoff rule [3]. When performing the reaction in boiling methanol in the presence of trifluoroacetic acid, the conversion depends on the percentage of the latter. In the solution of *O*-vinylacetoxime **I** in CCl_4 at 20–60ºC and in the absence of catalyst such reaction with methanol does not take place. The ν(C=C) band in the spectrum of this solution with excess of methanol remains unchanged. This allowed the use of methanol for determination of the centers of basicity in *O*-vinylacetoxime **I**. Unlike oxime **I**, the basicity of oxime **II** was determined upon its interaction not only with methanol but also with standard proton-donor, phenol. The data of quantum chemical calculations were used for analysis of the Δν(OH) values in the IR spectra of solutions. On the example of H-complexes of diethyl ether with methanol **XIX** and phenol **XX** it was shown

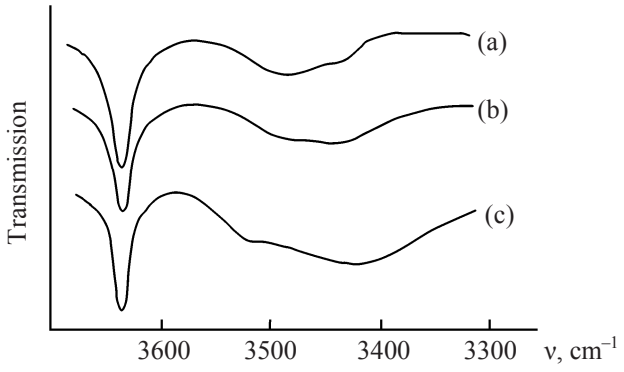


Fig. 4. IR spectra of *O*-vinylacetoxime **I** at (a) 25°C, (b) –40°C, and (c) of *O*-ethylacetoxime **II**, 25°C in CCl_4 solution with addition of methanol.

that the experimental values of Δν(OH) for them, equal to 148 and 277 cm^{-1}, respectively, are close to the theoretically calculated at the B3LYP/6-311G* level (140 and 264 cm^{-1}) [10].

The addition of *O*-ethylacetoxime **II** to the diluted solution of methanol in CCl_4 ($C \sim 10^{-4}$ M) leads to a decrease in the intensity of the stretching vibration band of free OH groups (3637 cm^{-1}) in the IR spectrum. Simultaneously, a wide absorption band of the associated OH groups (3422 cm^{-1}) with a shoulder at 3520 cm^{-1} appears in the spectrum (Fig. 4c). Upon heating of the solution to 40–50°C the intensity of the doublet band decreases with simultaneous increase in the intensity of the vibration band of free OH groups. The spectral shifts Δν(OH) of the maxima of the doublet band with respect to ν(OH) of free hydroxy group in this spectrum are equal to 117 and 215 cm^{-1} (Table). The best correspondence of these values to the calculated Δν(OH) in the H-complexes of oxime **II** with methanol having O···HO (118 cm^{-1}) (**X**) and N···HO (182 cm^{-1}) (**IX**) bonds suggests the predominant formation of two types of H-complexes of the 1:1 composition in solution. With this, the band at 3422 cm^{-1} belongs to the more stable H-complex **IX** with the N···HO bond, and its high-frequency shoulder, to H-complex **X** with the O···HO bond. In the spectrum of solution of methanol and oxime **II** in CH_2Cl_2 a similar doublet band with maximum at 3398 and shoulder at 3500 cm^{-1} is observed. A decrease in the temperature of the solution to –20°C results in an increase in the intensity of the low frequency component of the band, corresponding to H-complex **IX**, and disappearance of the high frequency component.

The addition of oxime **II** to the diluted solution of phenol in CCl_4 ($C \sim 10^{-4}$ M) results in the appearance (alongside the stretching vibration band of free OH groups of proton-donor at 3612 cm^{-1}) of a doublet band of associated OH groups with the components at 3397 and 3227 cm^{-1} of comparable intensity. The high frequency component can be assigned to stretching vibrations of the OH groups participating in the formation of the O···HO bonds since the spectral shift Δν(OH) of 215 cm^{-1} corresponds to the calculated value of 208 cm^{-1} for complex **XIII** (1:1) (Table 1). The Δν(OH) value of 385 cm^{-1} corresponding to the low frequency maximum is the most close to the calculated value of 319 cm^{-1} (**XII**) (1:1) for the OH groups participating in the formation of the N···HO bonds (Table 1).

Therefore, in inert media a dynamic equilibrium is observed between the free molecules of *O*-ethylacetoxime **II** and its H-complexes (methanol, phenol) of 1:1 composition of the two types: with the N···HO or O···HO bonds. Formation of H-complexes of oxime **II** of 1:2 composition **XI, XIV** is hardly probable since the calculated values of the spectral shifts for their O···HO, N···HO bonds do not correspond to the observed ones (see Table 1).

The addition of *O*-vinylacetoxime **I** to the diluted solution of MeOH in CCl_4 leads to a decrease in the intensity of the stretching vibration band of the free OH group of methanol and a wide band of associated OH groups with two maxima (3483 and 3438 cm^{-1}) (Figs. 4a, 4b). Their low frequency shift Δν(OH) with respect to the band of the free OH groups amounts to 154 and 199 cm^{-1} and corresponds to formation of the N···HO hydrogen bonds with two conformers (**I**-*ap,ap* and **I**-*ap,sp*) in compliance with the results of calculatioins for complexes **IIIa** and **IIIb** (see Table 1). For complexes with O···HO bonds **IVa** and **IVb** the calculated values of Δν(OH) are much less (63 and 73 cm^{-1}). Cooling of the solution of oxime **I** with methanol in CCl_4 to –40ºC leads to a strong increase in the intensity of the low frequency component of the doublet band, which belongs to more stable H-complex of the (**I**-*ap,sp*) conformer **IIIb**. The observed Δν(OH) values, as in the case of oxime **II**, do not correspond to the calculated for H-complexes of oxime **I** of 1:2 composition **Va** and **Vb** (see Table 1).

Therefore, oxime **I**, as distinct from oxime **II**, forms H-complexes with participation of only the nitrogen atom. This is due to diminished basicity of its

oxygen atom which according to calculations is twice as low as that of oxime **II**.

EXPERIMENTAL

O-Vinylacetoxime was synthesized by the earlier described procedure [14]. IR spectra from solutions of the compounds were obtained on a Specord 75 IR spectrophotometer. Quantum-chemical calculations were performed at the B3LYP/6-311G* level using the GAUSSIAN-03 package [15]. The geometry of molecular systems was fully optimized to energy minima with the accuracy of 10^{-5} au/Bohr. Positive eigenvalues of the Hessian matrix for all structures confirm that they belong to minima on the potential energy surface. The energy of formation of H-complexes (ΔE) was estimated as the difference between their total energies and the sum of energies of the components.

REFERENCES

1. Trofimov, B.A., Mikhaleva, A.I., Vasil'tsov, A.M., Schmidt, E.Yu., Tarasova, O.A., Morozova, L.V., Sobenina, L.N., Preiss, T., and Henkelmann, J., *Synthesis*, 2000, vol. 8, no. 4, p. 1125.
2. Zaitsev, A.B., Schmidt, E.Yu., Vasil'tsov, A.M., Mikhaleva, A.I., Morozova, L.V., Ushakov, I.A., Afonin, A.V., and Il'icheva, L.N., *Russ. J. Org. Chem. Engl. Transl*., 2003, vol. 39, no. 10, p. 1406.
3. Sohlberg, K., Leary, S.P., Owen, N.L., and Trofimov, B.A., *Vibrat. Spectrosc*., 1997, vol. 13, p. 227.
4. Sohlberg, K. and Dobbs, K.D., *J. Mol. Struct. (Theochem).,* 2002, vol. 577, p. 137.
5. Aksamentova, T.N., Knizhnik, A.V., Tarasova, O.A., Mikhaleva, A.I., and Trofimov, B.A., *Russ. Chem. Bull. Engl. Transl*., 1999, vol. 48, no. 9, p. 1573.
6. Shagun, V.A., Sinegovskaya, L.M., Toryashinova, D.-S.D., Tarasova O.A., and Trofimov, B.A., *Russ. Chem. Bull. Engl. Transl*., 2001, vol. 50, no. 5, p. 764.
7. Chipanina, N.N., Aksamentova, T.N., and Trofimov, B.A., *Russ. Chem. Bull. Engl. Transl*., 2000, vol. 49, no. 4, p. 601.
8. Kobychev, V.B., Vitkovskaya, N.M., and Trofimov, B.A., *J. Struct. Chem*., 2008, vol. 49, no. 2, p. 216.
9. Aksamentova, T.N., Chipanina, N.N., Mikhaleva, A.I., and Trofimov, B.A., *Russ. J. Gen. Chem. Engl. Transl*., 2008, vol. 78, no. 4, p. 585.
10. Sterkhova, I.V., Vokin, A.I., Oznobikhina, L.P., Chipanina, N.N., Shainyan, B.A., and Turchaninov, V.K., *Russ. J. Gen. Chem. Engl. Transl*., 2007, vol. 77, no. 2, p. 264.
11. Sinegovskaya, L.M. and Trofimov, B.A., *Russ. Chem. Rev. Engl. Transl*., 1996, vol. 65, no. 1, p. 1009.
12. Bzhezovskii, V.M., Kapustin, E.G., and Trofimov, B.A., *Russ. J. Gen. Chem. Engl. Transl*., 2003, vol. 73, no. 5, p. 731.
13. Trofimov, B.A., *Geteroatomnye proizvodnye atsetilena* (Heteroatomic Derivatives of Acetylene), Moscow: Nauka, 1981.
14. Tarasova, O.A., Korostova, S.E., Mikhaleva, A.I., Sobenina, L.N., Nesterenko, R.N., Shevchenko, S.G., and Trofimov, B.A., *Zh. Obshch. Khim*. 1994, vol. 30, no. 6, p. 810.
15. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda Y., Kitao, O., Nakai, H., Klene, M., Li X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, p., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, w., Wong, M.W.,