

Acid–Base Interactions in the Dichloroacetic Acid–*N,N*-Dimethylformamide System as Found from IR Spectroscopic Data

V. D. Maiorov, G. I. Voloshenko, and N. B. Librovich

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

e-mail: proton@chph.ras.ru

Received March 13, 2003

Abstract—Ion–molecule interactions in the dichloroacetic acid–*N,N*-dimethylformamide system in the concentration range from pure acid to pure base at 30°C were investigated by multiple attenuated total internal reflectance IR spectroscopy. It was found that, depending on the ratio between components in solution, 1 : 1 or 2 : 1 acid–base complexes with strong hydrogen bonds are formed. With an excess of the acid, protonation of the base does not occur. The intensity of continuous absorption at 2000 cm^{−1} is characteristic of quasi-ionic pairs with strong symmetrical hydrogen bonds. However, along with a continuous component, the spectra exhibited individual sharp peaks, which are typical of molecular complexes.

INTRODUCTION

A fundamental property of protons in solutions is the formation of ions and complexes with strong symmetrical hydrogen bonds [1, 2]. Catalytic properties of acid solutions are determined primarily by the structure and concentration of these species. The formation of uncharged 1 : 1 complexes with strong quasi-symmetrical hydrogen bonds is characteristic of many non-aqueous systems [3–6]. In particular, such complexes were found in the methanesulfonic acid (MSA)–dimethyl sulfoxide and trifluoroacetic acid–dimethylformamide (DMF) systems [3]. The interaction of weaker bases with acids can result in molecular complexes as, for instance, in the MSA–propylene carbonate [7] and dichloroacetic acid (DCA)–ethyl acetate (EA) [8] systems. The acidity function measurements [9] in systems containing acid–base complexes different in degree of proton transfer from the acid molecule to the base mol-

ecule showed that molecular complexes exhibit the highest ionizing ability. Therefore, it is important to have information on the conditions of their formation. This work deals with the complexation of dichloroacetic acid with *N,N*-dimethylformamide, the stronger base as compared with ethyl acetate.

EXPERIMENTAL

Dichloroacetic acid (puriss grade) and DMF (puriss grade) from Fluka with H₂O contents lower than 0.05 and 0.01%, respectively, were used. Solutions were prepared by a weight method. Molar concentrations were calculated from the measured densities of solutions (Table 1).

IR spectra were measured on a UR-20 spectrophotometer with a multiple attenuated total internal reflectance attachment [10]. A Ge prism with an incident

Table 1. Stoichiometric compositions and densities of dichloroacetic acid solutions in DMF at $T = 30 \pm 1^\circ\text{C}$

[DCA] ₀ , %	[DCA] ₀ ,	[DMF] ₀ ,	ρ , g/cm ³	[DCA] ₀ , %	[DCA] ₀ ,	[DMF] ₀ ,	ρ , g/cm ³
	mol/l	mol/l			mol/l	mol/l	
0	0	12.91	0.944	71.45	7.45	5.25	1.344
25.31	2.07	10.77	1.054	73.26	7.71	4.97	1.358
40.85	3.62	0.92	1.142	77.91	8.40	4.20	1.390
46.57	4.22	8.53	1.167	82.46	9.13	3.43	1.428
52.01	4.88	7.94	1.210	89.60	10.30	2.11	1.483
58.24	5.65	7.14	1.250	95.37	11.31	0.97	1.529
64.20	6.41	6.30	1.287	100.00	12.15	0.00	1.567
67.02	6.83	5.93	1.31				

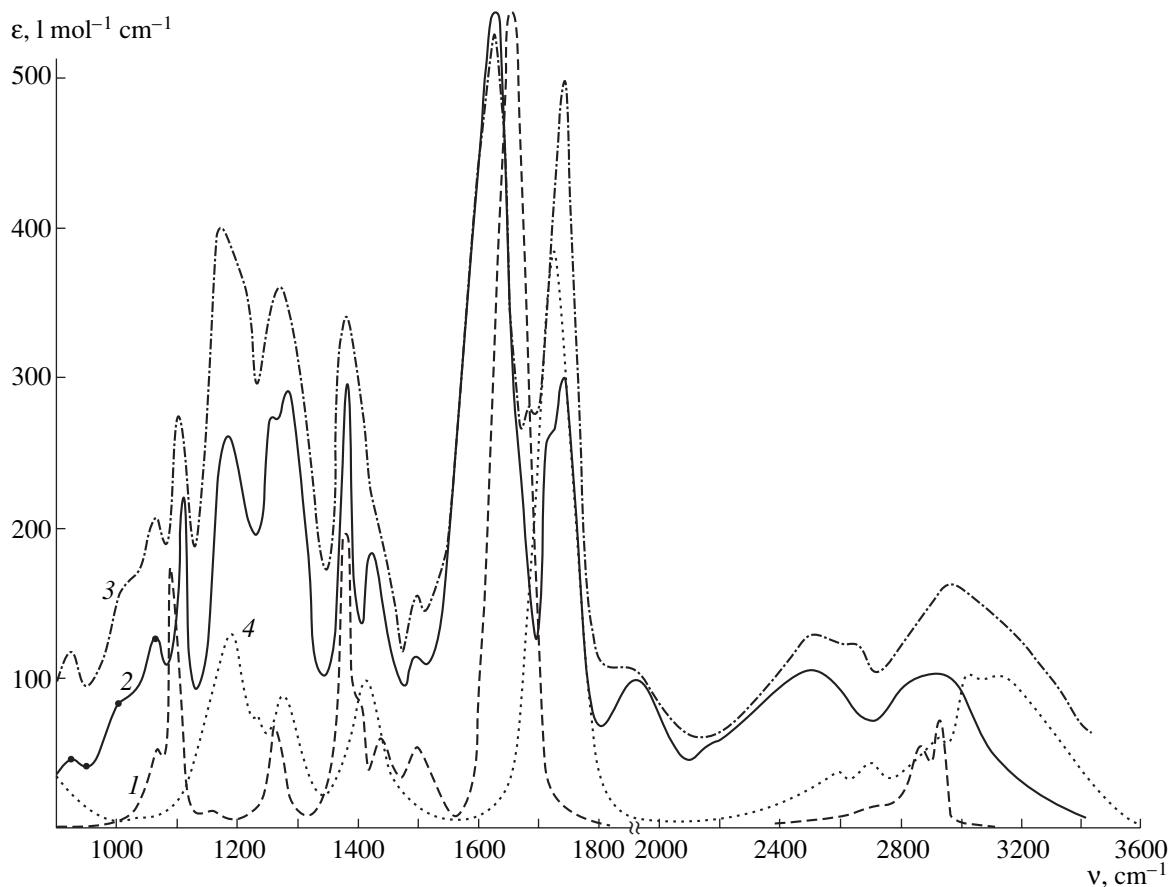


Fig. 1. IR spectra of DCA solutions in DMF: (1) 100% DMF, (2) 50 mol % DCA (K_1), (3) 66.7 mol % DCA (K_2), (4) 100% DCA.

angle of 30° was used. The test solution was placed in Teflon cells adjacent to the prism faces. The number of reflections was 4 or 8, depending on the filling of the cells. The effective thickness of the absorbing layer at 2000 cm^{-1} was equal to 2.02 or $4.06\text{ }\mu\text{m}$, respectively.

The spectra of the DCA-DMF system with DCA concentrations in the range 0–100% (Table 1) were measured in the frequency range 900 – 3800 cm^{-1} at 30°C . Absorbance was measured in reference to base lines or to the absorbance of an empty cell. The absorbance measurements were accurate to $\pm 7\%$.

The IR spectra of DCA and DMF (Fig. 1) involve a number of intense bands (ν, cm^{-1}) at 1193 ($\delta(\text{COH})$, $\nu_{\text{as}}(\text{C}-\text{C}-\text{O})$), 1275 ($\delta(\text{COH})$), 1415 ($\delta(\text{C}-\text{H})$), 1730 ($\nu(\text{C}=\text{O})$), and 3100 ($\nu(\text{O}-\text{H})$), which are characteristic of DCA [11], and at 1093 ($\delta(\text{NCH})$), 1255 ($\nu_{\text{as}}(\text{N}-\text{CH}_3)$), 1383 ($\nu(\text{C}-\text{N})$), and 1665 ($\nu(\text{C}=\text{O})$), which are characteristic of DMF [12], and also bands in the range 2850 – 3000 cm^{-1} assigned to the stretching vibrations of hydrogen atoms in $\text{C}-\text{H}$ (DCA and DMF) and in CH_3 groups (DMF).

RESULTS AND DISCUSSION

The addition of DCA to 100% DMF results in noticeable shifts of some absorption bands due to the

base molecules (1093 to 1110 cm^{-1} and 1665 to 1633 cm^{-1}), in the appearance of new bands (at 920 , 1010 , 1063 , 1930 , 2480 , and $\sim 2900\text{ cm}^{-1}$), and in an increase in background absorption in the range 900 – 1400 cm^{-1} (Fig. 1). The new and shifted bands reach their maxima at a $1:1$ ratio between the components of solutions (Fig. 2). This is indicative of the formation of a stable $1:1$ DCA-DMF complex (K_1) in solution. Bands due to OH stretching vibrations of the acid and the $\text{C}=\text{O}$ groups of the base molecules (1665 cm^{-1}) show the greatest changes. In an equimolar solution, these bands practically disappeared (Figs. 1, 3, 4).

If a $1:1$ complex is formed upon the addition of acid molecules to DMF, then in an excess of DMF, the absorbance at the frequency $\nu(D_\nu)$ is equal to the sum of the absorbance of K_1 complexes and the absorbance of uncomplexed DMF molecules:

$$D_\nu = \varepsilon_\nu^{\text{DMF}} l_\nu [\text{DMF}] + \varepsilon_\nu^{K_1} l_\nu [K_1], \quad (1)$$

where l_ν is the effective thickness of the absorbing layer at the frequency ν .

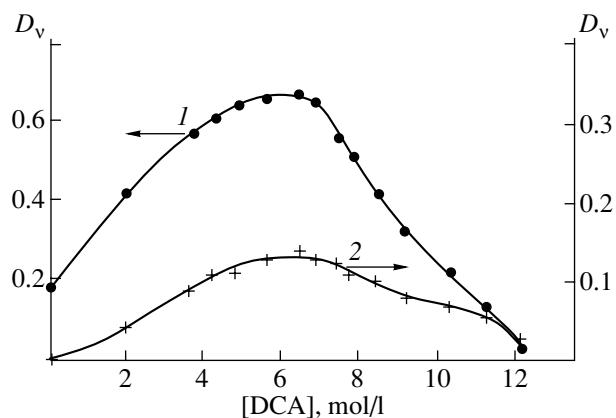


Fig. 2. Dependence of the absorbance of complexes at (1) 1633 and (2) 2200 cm^{-1} on the concentration of DCA.

Since a DCA molecule is tightly bound to a single DMF molecule,

$$[\text{K}_1] = [\text{DCA}]_0,$$

$$[\text{DMF}] = [\text{DMF}]_0 - [\text{DCA}]_0,$$

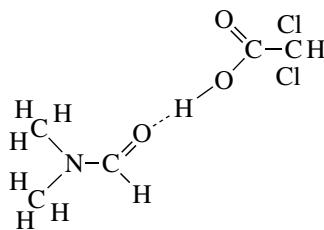
where $[\text{DCA}]_0$ and $[\text{DMF}]_0$ are the stoichiometric concentrations of DCA and DMF, respectively.

From Eq. (1), we obtain

$$D_v/[\text{DMF}] = \varepsilon_v^{\text{DMF}} l_v + \varepsilon_v^{\text{K}_1} l_v ([\text{K}_1]/[\text{DMF}]_0). \quad (2)$$

For bands at 1093 and 1383 cm^{-1} , linear dependence (2) holds to an equimolar ratio between the components. This lends support to the formation of a K_1 complex of one acid molecule and one base molecule. Because the complex formation resulted in the strongest changes of bands assigned to the stretching vibra-

tions of the O-H group in the acid molecule and the C=O group in the DMF molecule, we can suggest the following structure of the K_1 complex:



Hydrogen bonds of this kind between acid molecules and the C=O groups of DMF molecules were found in the 1 : 1 acid-base complexes of DMF with HCl by X-ray diffraction analysis. The formation of H-bonds at the nitrogen atom was not observed [13]. The same result was obtained from the *ab initio* calculations of DMF complexes with HCl [14].

For some bands, the concentration dependence of the absorbance exhibited a maximum or an inflection point at a 2 : 1 ratio between the components. This is true, first of all, for the bands at 1093 and 1383 cm^{-1} of the base (Fig. 3) and the bands at 1193 and 1420 cm^{-1} of the acid (Fig. 4), and also for the background absorption at $\nu < 1400 \text{ cm}^{-1}$. These findings are indicative of the formation of DMF · 2DCA complexes (K_2) in an excess of acid.

The addition of the acid to an equimolar solution containing only 1 : 1 complexes gives rise to the band of O-H stretching vibrations of the acid molecules in the spectrum (see Fig. 4); in this case, absorption coefficients measured at 3100 and 3200 cm^{-1} coincide with those for the pure acid (see Table 2). Consequently, the OH group of the second acid molecule in the K_2 complex is not hydrogen-bonded to the DMF molecule, and the nitrogen atom of the base is not involved in hydro-

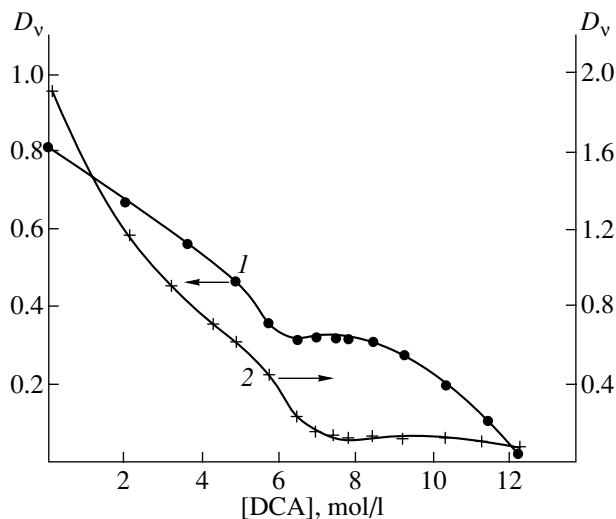


Fig. 3. Dependence of the absorbance of DMF at (1) 1093 and (2) 1665 cm^{-1} on the concentration of DCA.

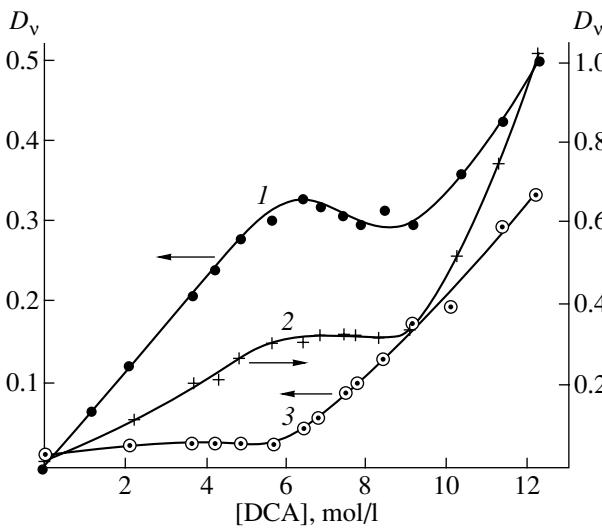


Fig. 4. Dependence of the absorbance of DCA at (1) 1193, (2) 1730, and (3) 3100 cm^{-1} on the concentration of DCA.

Table 2. Absorbance of DCA at 1730, 3100, and 3200 cm^{-1} and of DMF at 1665 cm^{-1} at various compositions of the DCA-DMF system a $T = 30 \pm 1^\circ\text{C}$

[DCA] ₀ , mol/l	[DMF] ₀ ,	D_{3100}	n_{3100}^*	D_{3200}	n_{3200}	D_{1730}	n_{1730}	D_{1665}	n_{1665}^{**}
12.15	0.00	0.333	—	0.301	—	1.030	—	—	—
11.31	0.97	0.294	0.7	0.264	0.8	0.768	2.3	—	—
10.30	2.11	0.239	0.8	0.220	0.7	0.569	1.7	—	—
9.13	3.43	0.170	0.9	0.156	0.9	0.367	1.4	—	—
8.40	4.20	0.132	0.9	0.111	1.0	0.307	1.1	—	—
7.71	4.97	0.105	0.8	0.082	0.9	0.329	0.8	—	—
7.45	5.25	0.088	0.8	0.067	0.9	0.330	0.7	—	—
6.83	5.93	0.057	0.8	0.032	0.9	0.349	0.5	—	—
6.41	6.30	0.043	0.8	0.014	0.9	0.291	0.5	0.244	0.7
5.65	7.14	—	—	—	—	—	—	0.461	0.7
4.88	7.94	—	—	—	—	—	—	0.647	0.7
4.22	8.53	—	—	—	—	—	—	0.743	0.9
3.62	0.92	—	—	—	—	—	—	0.935	0.8
2.07	10.77	—	—	—	—	—	—	1.198	1.3
0	12.91	—	—	—	—	—	—	1.942	—

* $n_v = ([\text{DCA}]_0 - D_v/\epsilon_v)/[\text{DMF}]_0$, where ϵ_v is determined from the spectrum of 100% DCA ($v = 1730, 3100, 3200 \text{ cm}^{-1}$).

** $n_v = ([\text{DMF}]_0 - D_v/\epsilon_v)/[\text{DCA}]_0$, where ϵ_v is determined from of 100% DMF ($v = 1665 \text{ cm}^{-1}$).

gen bonding. On the other hand, in the formation of K_2 , the greatest changes are observed in the $\delta(\text{NCH})$ band of the DMF molecule at 1093 cm^{-1} (Fig. 3) and in the bands at 1193 and 1730 cm^{-1} assigned to the $\nu_{\text{as}}(\text{C}-\text{C}-\text{O})$ and $\nu(\text{C}=\text{O})$ vibrations in DCA, respectively (Fig. 4, Table 2). This is evidence for the coordination of the $\text{C}=\text{O}$ group of the second acid molecule in K_2 with the hydrogen atom of the $\text{C}-\text{H}$ bond in the DMF molecule.

Under the assumption that, in solutions containing 50–67 mol % DCA, the acid and the base are fully bound into K_1 and K_2 complexes, the absorbance at the frequency v (D_v) is the sum of the absorbances of these complexes:

$$D_v = \epsilon_v^{K_1} l_v [K_1] + \epsilon_v^{K_2} l_v [K_2]. \quad (3)$$

Hence, it follows that

$$D_v/[K_1] = \epsilon_v^{K_1} l_v + \epsilon_v^{K_2} l_v ([K_2]/[K_1]), \quad (4)$$

where $[K_1] + [K_2] = [\text{DMF}]$ and $[K_2] = [\text{DCA}]_0 - [\text{DMF}]_0$.

The absorbance D_v at $[\text{DCA}]_0/[\text{DMF}]_0 \geq 2 : 1$ is the sum of the absorbances of free acid molecules and K_2 complexes:

$$D_v = \epsilon_v^{\text{DCA}} l_v [\text{DCA}] + \epsilon_v^{K_2} l_v [K_2], \quad (5)$$

where $[K_2] = [\text{DMF}]_0$ and $[\text{DCA}] = [\text{DCA}]_0 - 2[\text{DMF}]_0$.

On rearrangement, Eq. (5) acquires the form

$$D_v/[\text{DCA}] = \epsilon_v^{\text{DCA}} l_v + \epsilon_v^{K_2} l_v [K_2]/[\text{DCA}]. \quad (6)$$

For the bands at $1093, 1193, 1383$, and 1730 cm^{-1} , functions (4) and (6) are linear in the DCA concentration ranges 50–67 and 67–100 mol %, respectively. Calculated coefficients for K_1 and K_2 complexes and for the initial components are listed in Table 3. The absorption coefficients ϵ^{K_2} and ϵ^{K_1} obtained from Eqs. (2), (4), and (6) are consistent.

From the previous, it follows that the K_2 complex is formed by the attachment of the carbonyl oxygen atom of the acid molecule to the hydrogen atom of the $\text{C}-\text{H}$ group of the DMF molecule in the K_1 complex. This is consistent with the fact that the absorption coefficient for the vibrational $\nu(\text{O}-\text{H})$ band of the acid molecules,

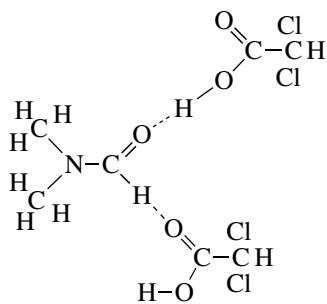
Table 3. Absorption coefficients of the complexes of DMF with DCA at $T = 30 \pm 1^\circ\text{C}$

ν^*, cm^{-1}	$l_\nu, \mu\text{m}$	$\epsilon, 1 \text{ mol}^{-1} \text{ cm}^{-1}$			
		DMF	DMF · DCA	DMF · 2DCA	DCA
1093	3.70	170	149	214	8.1
1193	3.40	0	156	94**	121
1383	2.92	164	195	158	24
1730	2.34	17	222	154**	359

* Absorbance at 1193, 1383, and 1730 cm^{-1} was measured with reference to baselines, and absorbance at 1093 cm^{-1} , with reference to empty cells.

** For bands assigned to acid molecules incorporated in K_2 , absorption coefficients were calculated on a DCA molecule basis.

which complex with K_1 to form K_2 , is identical to that for pure DCA. The *ab initio* calculations [14] for the DMF–HCl system also showed that the hydrogen atom of the C–H group rather than the nitrogen atom of the base is involved in hydrogen bonding with the acid molecule.



Absorption at 2000 cm^{-1} is due to the wing of the band of K_1 complexes with a maximum at 1930 cm^{-1} . Therefore, the intensity of continuous absorption was measured at the minimum located at 2100 cm^{-1} . At a 1 : 1 ratio between the components, $\epsilon_{2100} = 65 \pm 5 \text{ l mol}^{-1} \text{ cm}^{-1}$. This value is characteristic of uncharged 1 : 1 complexes with strong quasi-symmetrical hydrogen bonds. The formation of strong quasi-symmetrical hydrogen bonds is also supported by the disappearance of bands due to O–H vibrations in the acid and C=O vibrations in the base [3–6].

On the other hand, background absorption in the frequency range 900–1500 cm^{-1} is much (approximately two times) weaker than that for systems containing uncharged complexes with strong quasi-symmetrical hydrogen bonds [3, 4]. Individual bands of the 1 : 1 complex are of high intensity and show no smearing, which is characteristic of molecular complexes.

The choice of test materials was based on the assumption that, in contrast to molecular complexes in the DCA–ethyl acetate system, DCA–DMF complexes will have strong symmetrical hydrogen bonds, because DMF is a stronger base. The IR spectra of such complexes are characterized by continuous absorption and

strongly smeared individual bands. This is due to strong interplay between the skeletal vibrations of molecules that form a proton disolvate and the vibrations of the proton in the central symmetrical (quasi-symmetrical) hydrogen bond [1, 2]. It is likely that the structure of DCA, in particular, the presence of chlorine atoms, prevents the interplay between the skeletal vibrations and the proton vibrations in the bridge of a strong symmetrical hydrogen bond. Another explanation is that, in the DMF–DCA complex, the potential of the strong hydrogen bond is not symmetrical.

Thus, we found that, depending on the ratio of components in solution, 1 : 1 and 2 : 1 acid–base complexes with strong hydrogen bonds are formed. In an excess of acid, protonation of the base does not occur. The intensity of continuous absorption at 2000 cm^{-1} is characteristic of quasi-ionic pairs with strong symmetrical hydrogen bonds. At the same time, along with the continuous component, the spectra involve individual sharp peaks typical of molecular complexes.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 02-03-32174.

REFERENCES

1. Yukhnevich, G.V., Tarakanova, E.G., Mayorov, V.D., and Librovich, N.B., *J. Mol. Struct.*, 1992, vol. 265, p. 237.
2. Yukhnevich, G.V., Tarakanova, E.G., Maiorov, V.D., and Librovich, N.B., *Usp. Khim.*, 1995, vol. 64, no. 10, p. 963.
3. Maiorov, V.D., Kislina, I.S., Voloshenko, G.I., and Librovich, N.B., *Izv. Akad. Nauk, Ser. Khim.*, 2000, no. 9, p. 1537.
4. Maiorov, V.D. and Kislina, I.S., *Khim. Fiz.*, 1992, vol. 11, no. 5, p. 660.
5. Pankov, A.A., Borovkov, V.Yu., and Kazanskii, V.B., *Khim. Fiz.*, 1985, vol. 4, p. 249.

6. Mikheev, V.A., Sokornova, T.V., and Shraiber, V.M., *Zh. Prikl. Spektrosk.*, 1992, vol. 57, nos. 3–4, p. 227.
7. Maiorov, V.D., Voloshenko, G.I., Kirilova, A.P., and Librovich, N.B., *Izv. Akad. Nauk, Ser. Khim.*, 1999, no. 2, p. 313.
8. Maiorov, V.D., Voloshenko, G.I., and Librovich, N.B., *Kinet. Katal.*, 2002, no. 6, p. 940.
9. Kislina, I.S. and Sysoeva, S.G., *Izv. Akad. Nauk, Ser. Khim.*, 2001, no. 6, p. 961.
10. Harrick, N.J., *Internal Reflection Spectroscopy*, New York: Wiley, 1967.
11. Fukushima, K. and Zwolinski, B., *J. Chem. Phys.*, 1969, vol. 50, no. 2, p. 737.
12. Jao, T.C., Scott, I., and Steel, D., *J. Mol. Spectrosc.*, 1982, vol. 92, no. 1, p. 1.
13. Kislina, I.S., Sysoeva, S.G., Librovich, N.B., Temkin, O.N., Eremenko, I.L., and Nefedov, S.E., *Dokl. Akad. Nauk*, 1998, vol. 360, no. 5, p. 649.
14. Kislina, I.S., Librovich, N.B., Maiorov, V.D., Tarakanova, E.G., and Yukhnevich, G.V., *Kinet. Katal.*, 2002, vol. 43, no. 5, p. 718.