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Conformations of the Ester. VII. The Conformations of Chloroformates[1]

Michinori Ōki and Hiroshi Nakanishi
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

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In earlier papers from this laboratory, it has been shown that acetates[2] and other carboxylate esters exist as *s-trans* conformers only, whereas two conformational isomers (*s-trans* and *s-cis*) exist in some formates,[3] carbamates,[4] carbonates,[5] and monothiocarbonates.[1]

In formates, the *s-trans* conformer is more stable than the *s-cis*, while in the others, which have an electronegative atom connected with the carbonyl group, the *s-cis* conformer is more stable than the *s-trans*.

s-trans *s-cis*

X = CH_3, H, NR_2, OR, SR, Cl

Since the electronegativity of chlorine is greater than that of nitrogen and oxygen, it seemed that it would be of interest to study the case of chloroformates. Since the chlorine atom is larger than nitrogen and oxygen, the steric repulsion between X (N or O) and R in the *s-cis* conformation is expected to be smaller in carbamates and carbonates than that between Cl and R in chloroformates. Thus, the steric and electronic effects may counterbalance each other in chloroformates in determining the conformational preference to some extent.

As to the conformation of haloformates, several papers have been published. The haloformates had most commonly been reported to exist as *s-cis* conformers, judging from the data of dipole moments[6-8] and NMR spectra.[8] However, an exception has been reported by O'Gorman *et al.*,[9] who postulated that the conformation is *s-trans*; they based their postulate on the electron scattering spectral data.

From our experience so far, it seems that the infrared spectral study may throw light on this problem. Thus, the infrared spectra of some chloroformates have been carefully observed, and NMR spectra have been measured at low temperatures.

Experimental

Methyl and ethyl chloroformates were of commercial origin. Isopropyl chloroformate was prepared from phosgene and isopropyl alcohol and phenyl chloroformate from phosgene and sodium phenoxide. The esters were purified by distillation before the measurements. The purity was checked by means of the NMR spectra and the infrared spectra. The spectra were measured with previously-described spectrometers.[5]

Results and Discussion

Infrared Spectra. There have been several reports on the carbonyl stretching absorption of chloroformates, but no one has yet discussed the shape of the carbonyl absorption. The results obtained with carbon tetrachloride and acetonitrile solutions are shown in Table 1. Apparently, methyl, ethyl, and isopropyl chloroformates show two carbonyl absorptions. Since the solvent effect is not very large, the bifurcation of the carbonyl absorption may not originate from Fermi resonance,[10] but from the existence of the *s-cis* and *s-trans* conformers.

TABLE 1. CARBONYL ABSORPTION OF CHLOROFORMATES $ClCO_2R$

Compound (R)		Solvent			
		CCl_4 $c=0.0004$ mol/*l*		CH_3CN $c=0.02$ mol/*l*	
I	Me	1770cm^{-1}	(266)	1767cm^{-1}	(277)
		1786	(613)	1786	(1363)
II	Et	1765	(36)	1768	(35)
		1778	(1161)	1779	(1021)
III	*i*-Pr	1761	(64)	1763	(64)
		1777	(1140)	1777	(1461)
IV	Ph	1790	(1477)	1788	(1106)

The dipole moments of the two conformers are calculated to be 1.6 D for the *s-trans* and 2.0 D for the *s-cis*. Since the *s-cis* conformer is more polar than the *s-trans*, the population of the former will become greater in the polar solvent than in the nonpolar. Table 1 shows that the intensity of the band at the higher frequency becomes larger in acetonitrile than in carbon tetrachloride, indicating that the band at the higher frequency may be assigned to the *s-cis* conformer. This assignment is also in accordance with the consideration of the arrangement of the bond dipoles (see the figure below): apparently, the stretching of the carbonyl bond in the *s-cis* conformation needs more energy. All of these results are consistent with the idea that the *s-cis* conformer is more stable than the *s-trans* in chloroformates.

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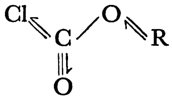
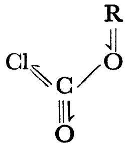
[1] Part VI: M. Ōki and H. Nakanishi, This Bulletin, in press.
[2] M. Ōki and H. Nakanishi, *ibid.*, **44**, 3144 (1971).
[3] M. Ōki and H. Nakanishi, *ibid.*, **43**, 2558 (1970).
[4] M. Ōki and H. Nakanishi, *ibid.*, **44**, 3148 (1971).
[5] M. Ōki and H. Nakanishi, *ibid.*, **44**, 3419 (1971).
[6] S. Mizushima and M. Kubo, *ibid.*, **13**, 174 (1938).
[7] E. Bock and D. Iwacha, *Can. J. Chem.*, **45**, 3177 (1967).
[8] E. Bock, D. Iwacha, H. Hutton, and A. Queen, *ibid.*, **46**, 1645 (1968).
[9] J. M. O'Gorman, W. Shand, Jr., and V. Shomaker, *J. Amer. Chem. Soc.*, **72**, 4222 (1950).
[10] The solvent effect on the intensities of the carbonyl absorptions is very large if the bifuraction has its origin at the Fermi resonance. The detailed discussions were given in a previous paper.[2]


s-trans


s-cis

Methyl chloroformate has two absorptions in the carbonyl overtone region, at 3538 cm^{-1} ($\varepsilon=6.3$) and 3506 cm^{-1} ($\varepsilon=0.32$), in crabon tetrachloride ($c=0.01$ mol/l). This result lends further support to the idea that there are two conformational isomers in chloroformates. If the origin of the bifurcation of the carbonyl band were Fermi resonance, there would have been only one absorption in the overtone region.

Nuclear Magnetic Resonance Spectra. The NMR spectra of methyl chloroformate were measured at various temperatures in CS_2–CH_2Cl_2. A sharp singlet of methyl protons at 3.95 ppm from TMS is observed at room temperature, whereas the peak height decreases as the temperature is lowered. The peak height at −100°C is about a half of that at 23°C, whereas the peak height of standard TMS remains almost unchanged. This broadening of the methyl peak can best be interpreted by assuming the existence of conformational isomers.

The results of the infrared and NMR spectra and the discussions given above clearly show that alkyl formates have two conformers and that the *s-cis* conformer is more stable than the *s-trans*. Since the chlorine atom (1.80 Å)[11] is larger than hydrogen (1.2 Å) and a little smaller than the methyl group (2.0 Å), the *s-trans* conformation should be favored over the *s-cis* in view of the steric requirement. Therefore, the fact that the *s-cis* conformer is more stable in reality suggests that the electronic effect is the most important factor in determining the conformational preference.

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[11] The numbers in parentheses refer to the van der Waals radii.