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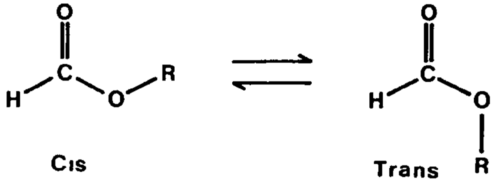
CONFORMATIONAL POPULATIONS AND ROTATIONAL BARRIERS IN ESTERS

T. Bruce Grindley

Department of Chemistry, Dalhousie University,
Halifax, Nova Scotia, B3H 4J3, Canada.

Abstract: The trans conformations of methyl, ethyl and isopropyl formate were shown to be present in equilibrium in a polar solvent with the cis conformations to significant (> 1% at 230 K) but much lower extents than for t-butyl formate; rotational barriers for the former compounds are greater.

Extensive investigation of the conformational isomerism in esters arising from rotation about the C-O single bond has demonstrated that the planar cis conformation is the major conformer but evidence about the relative importance of the planar trans conformation has been contradictory.[1]



	R		R
1	Me	2	Et
3	iPr	4	t-Bu

Direct proof of the presence of the trans conformation has been obtained only for t-alkyl formates by n.m.r. spectroscopy[2-4] and a search for the trans conformer of simpler formates was unsuccessful.[4] Over the last few years, there has been considerable theoretical interest in the extent and cause of the cis preference in esters and in many types of related polar compounds like nitriles, enol ethers, amides, carboxylic acids and allyl anions[5-10]. In this publication, we report definitive evidence for measurable populations of the planar trans conformations of methyl, ethyl and isopropyl formate (1-3 respectively) in solution and also report rotational barriers for these compounds.

The 62.8 MHz ^{13}C n.m.r. spectra of 1-3 and of t-butyl formate (4) as 20% solutions in 1:1 mixtures of dimethylformamide and acetone-d_6 were recorded over ranges of temperatures from 163 K to ambient. In each case, the signals for all the carbon atoms of the trans isomer were clearly observed in the lower temperature spectra, although for methyl formate, only 0.3% of the minor isomer was present at 190 K. The ^{13}C chemical shifts are listed in Table 1. The signals for all carbons of the cis isomers are upfield of those of the trans isomers, except for that of the ethereal carbon of the t-butyl derivatives Similar reversals of order have been noted when the ^{15}N and ^{1}H chemical shifts

Table 1 ^{13}C NMR Chemical Shifts for Formates[a] (HCOOR)

R	$\underline{C}$=O			O-$\underline{C}$			C-$\underline{C}$		
	cis	trans	Δδ	cis	trans	Δδ	cis	trans	Δδ
Me[b]	163.3	167.1	3.8	51.0	55.5	4.5	-	-	-
Et[b]	162.8	166.5	3.7	60.1	61.7	4.6	14.2	15.8	1.7
iPr[c]	162.2	165.8	3.6	67.4	72.7	5.3	21.7	22.9	1.2
t-Bu[d]	164.3	167.3	3.0	83.2	82.1	-1.1	29.7	30.6	0.9

[a] chemical shifts in p.p.m. from internal TMS measured on 20% solutions in 1:1(v:v) mixtures of DMF and acetone-$\underline{d}_6$ [b] at 190 K [c] at 193 K [d] at 163 K)

for the cis and trans conformational isomers of tertiary alkyl formamides have been compared with those of other alkyl formamides[11,12]. Populations of the two isomers were obtained by integration of the low temperature spectra. Errors in the ΔG^0 values obtained are the standard deviations of the values from the signals for the three types of carbon atoms (two for methyl formate).

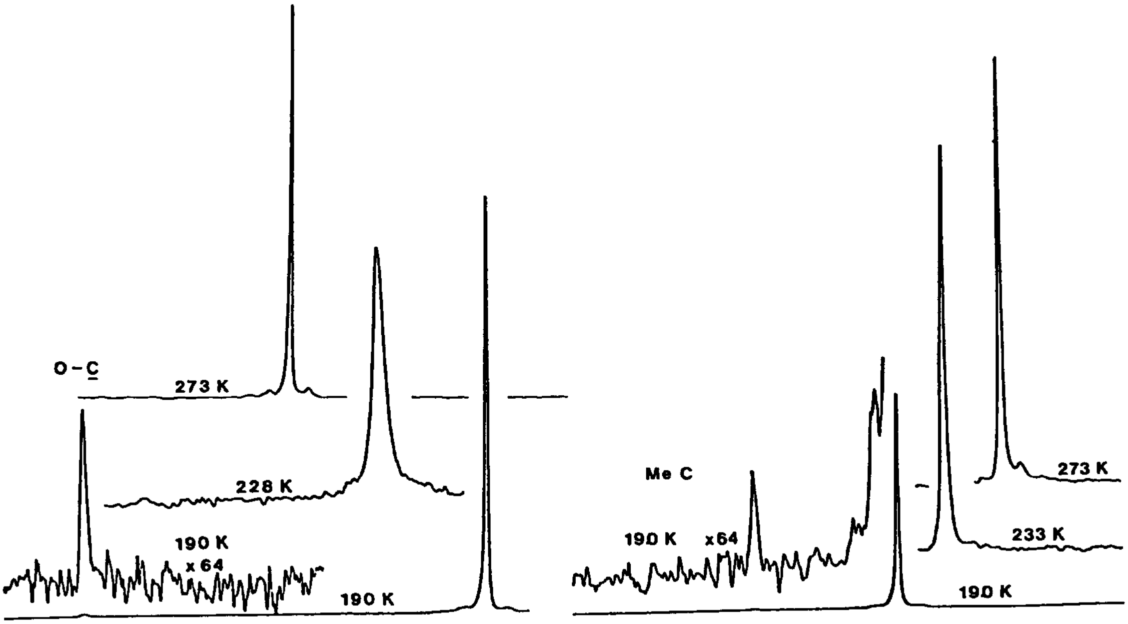


Fig. Temperature variation in portions of the 62.8 MHz ^{13}C nmr spectra of ethyl formate (2). The spectra to the left show the signals of the ethereal carbon, those to the right the signals of the methyl carbon. Spectra at different temperatures are displaced.

As the temperatures were raised, in all cases the signals for the minor isomers coalesced with those of the major isomers[13]. The figure shows the temperature variation of the regions of the spectra of ethyl formate which contain the signals of the ethereal and methyl carbons. For each carbon, spectra are shown below coalescence, at the temperature of maximum broadening and in the region of fast exchange. As noted earlier[14], the magnitude of the broadening observed is directly related to the chemical shift difference between the exchanging signals. The line shapes observed were simulated using a program[15] for two-site exchange. Chemical shifts for simulated spectra were obtained by a linear least squares extrapolation of the values obtained from several spectra below coalescence. Populations for simulated spectra were obtained from the low temperature ΔG^0 values by assuming ΔS^0 was zero. Satisfactory matches between simulated and observed spectra were obtained using this procedure for all formates except the methyl derivative. For this compound, the population of the minor isomer near coalescence had to be increased in order to obtain sufficient broadening to match the observed spectra. The rate constants obtained were used in an Eyring plot to obtain kinetic parameters. These values and the thermodynamic parameters are shown in Table 2.

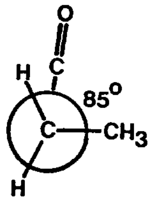
Table 2 Equilibrium and Activation Parameters ($kJ\text{-}mol^{-1}$)

Compound	$\Delta G^0 (c \rightarrow t)$[a]	$\Delta G^{\dagger} (c \rightarrow t)$[b]	$\Delta G^{\dagger} (t \rightarrow c)$[b]
1	9.0 ± .7[c]	41.5 ± .3	33.3 ± .3
2	7.0 ± .4	42.4 ± .2	35.4 ± .2
3	5.7 ± .3	42.4 ± .1	36.8 ± .1
4	2.0 ± .1[d]	36.4 ± .1[e]	34.6 ± .1[e]

[a] at 190 K [b] at 220 K [c] at 230 K, $\Delta G^0 = 8.1 \pm .7$

[d] at 168 K [e] at 190 K

There is probably more than one cause of the observed greater stability of the _cis_ conformation of formates. Since the preferred conformation of formic acid is also _cis_,[7] this arrangement of the $O{=}\overset{|}{C}{-}O{-}$ fragment must be more stable than the _trans_, probably because of repulsive electrostatic interactions in the latter conformation[8]. However, the greater stability of the same conformation of N-monoalkylformamides[16], where the above effect is not important, indicates that the _syn_ orientation of an _N_- or _O_- alkyl group with the carbonyl group also confers stability. This stabilization may be attributed to hyperconjugation[9,10] or possibly to attractive electrostatic effects.[6] Steric factors are also important and probably cause both the lower relative population of the _cis_ conformation of 4 and the lower barrier to rotation from this conformation of 4 as compared to those of 1-3. Riveros and Wilson[17] have shown that _cis_ ethyl formate prefers an _anti_ conformation of the ethyl



groups by 0.8 KJ mol^{-1} over a *gauche* conformation which has a CCOC torsional angle of 85° to avoid repulsive steric effects. Of the *cis* conformations of the four compounds considered here, only that of the t-butyl derivative need have two *gauche* groups and only in this conformation must the two *gauche* interactions be over equal torsional angles close to 60°. Thus, this conformation of 4 is considerably destabilized and the *trans* conformation is present to a much greater extent for 4 than for 1-3.

The *trans* conformations of esters with substituents on the carbonyl carbon will have additional steric interactions which will make their observation by n.m.r. spectroscopy extremely difficult.

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Footnotes and References

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