The Infrared Carbonyl Band Intensity in Some Substituted Ethyl Acetates

BY THEODORE L. BROWN

The intensity of infrared absorption due to the carbonyl band has been studied for a series of substituted ethyl acetates of the form $RCOOC_2H_5$. It is found that the group R affects the intensity as a result both of its steric and inductive properties. Increased electron-withdrawal, as measured by the polar substituent constant, σ^*, results in a lowered intensity. The presence of bulky groups *cis* to the carbonyl also produces a lowered intensity, principally as a result of van der Waals repulsion. Where barriers to internal rotation result in the presence of rotational isomers, the distribution of isomers can be determined and separate intensity values assigned.

Introduction

Several correlations have been established recently between infrared intensity and molecular reactivity parameters.[1-5] The present investigation was initiated in order to determine what relationship, if any, exists between the carbonyl intensity in compounds of the form $RCOOC_2H_5$, where R is an aliphatic group, and the properties of the group R. R can be expected to affect the intensity principally as a result of its inductive properties, as measured by the polar substituent constant, σ^*.[6] In addition, however, it may exert a steric effect.

Experimental

Materials.—Reagent grade carbon tetrachloride and chloroform were dried with powdered magnesium sulfate prior to use. Practical grade acetonitrile was refluxed with phosphorus pentoxide and then fractionally distilled. The esters were all obtained commercially and were carefully dried and fractionated prior to use.

Procedure.—The spectra were measured with a Perkin-Elmer Model 21 spectrometer fitted with sodium chloride optics. Slit openings of 0.025 and 0.035 mm. were employed, the larger with the acetonitrile solutions. A cell of 0.100 cm. thickness was used. The curves were integrated numerically in most instances, although graphical integration also was used for a few of the curves. At least four determinations were made on samples of varying concentration for each compound. The values of intensity were plotted vs. log $(I_0/I)_{max}$; the best straight line was then extrapolated to zero absorption to obtain the correct value for intensity. A definite concentration effect was observed in all instances. Measurements on separately purified samples of a few compounds showed that the value obtained for the intensity could be reproduced to within 0.03 intensity unit.[7] The spectrometer was frequency-calibrated by measurement of water vapor absorption. The reported values are considered correct to within 2 cm.$^{-1}$.

The integration interval chosen was about 90 cm.$^{-1}$ in those instances in which a single peak was observed. Where the absorption consisted of a double peak the interval was taken as extending to 40 cm.$^{-1}$ on each side of the nearer peak. This was done in an attempt to make any wing correction the same for all the compounds studied.[8] No wing corrections were applied in the present work. The absence of overlapping bands was indicated by the fact that the absorption had dropped to nearly zero at the edge of the integration interval.

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(2) T. L. Brown, THIS JOURNAL, **80**, 794 (1958).

(3) H. W. Thompson, R. W. Needham and D. Jameson, *Spectrochim. Acta*, **9**, 208 (1957).

(4) T. L. Brown, *Chem. Revs.*, in press.

(5) P. J. Stone and H. W. Thompson, *Spectrochim. Acta*, **10**, 17 (1957).

(6) R. W. Taft, in "Steric Effects in Organic Chemistry," M. S. Newman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1956.

(7) An intensity unit is taken as 1×10^4 mole^{-1} liter cm.$^{-2}$.

(8) D. A. Ramsay, THIS JOURNAL, **74**, 72 (1952).

Results

The results of intensity measurements on a number of esters are shown in Table I. In cases where a single absorption peak was observed the band shape was symmetrical. For the other compounds the band shape could be resolved easily as the sum of two symmetrical bands. The frequencies of these two bands are listed in the first two columns after the compound name. In the third column the ratio of the optical density, $\alpha = \log (I_0/I)_{max}$, of the high frequency band to that for the low frequency band is listed for the cases where applicable. In the fourth column is listed the total intensity, A.

Discussion

The splitting of the carbonyl absorption in esters of the type listed in Table I has been attributed to rotational isomerism as a result of an unsymmetrical arrangement of substituents on the group R.[9] It is to be expected that there are rotational isomers from the results of many studies on similar carbonyl compounds.[10,11] The fact that single

TABLE I

INTENSITY RESULTS FOR SOME ALIPHATIC ESTERS OF THE FORM $RCOOC_2H_5$ IN VARIOUS SOLVENTS

Group	ν_1(cm.$^{-1}$)	ν_2(cm.$^{-1}$)	α_1/α_2	A^a
CCl_4				
CH_3	..	1742	..	3.45
H	..	1741	..	3.34
$C_2H_5OCH_2$	1758	1736	1.94	2.95
CH_2Br	1760	1742	0.33	2.82
CH_2CN	..	1756	..	3.24
CH_2Cl	1767	1742	0.90	2.85
$CHCl_2$	1772	1750	0.93	2.74
CHF_2	1780	1766	1.52	2.87
CCl_3	1769	..	..	2.55
CH_3CN				
CH_2CN	..	1750	..	3.45
CH_2Cl	1758	1736	1.78	2.98
$CHCl_2$	1765	1751	2.04	2.94
CCl_3	1767	..	..	2.62
$CHCl_3$				
CH_2Cl	1755	1736	1.60	3.13
$CHCl_2$	1762	1745	1.45	3.13
CCl_3	1765	..	..	2.98

^{a} Intensity in units of 1×10^4 mole^{-1} liter cm.$^{-2}$.

(9) M. L. Josien and R. Callas, *Compt. rend.*, **240**, 1641 (1955).

(10) S. Mizushima, "Structure of Molecules," Academic Press, Inc., New York, N. Y., 1953.

(11) S. Mizushima, T. Shimanouchi, I. Ichishima, T. Mayazawa, I. Nakagawa and T. Araki, THIS JOURNAL, **78**, 2038 (1956).
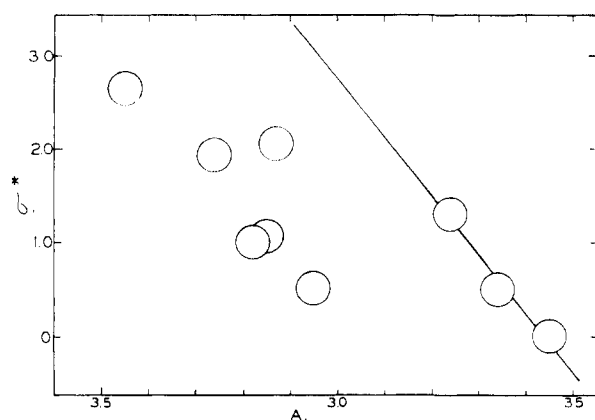
Fig. 1.—Total carbonyl intensity *vs.* the polar substituent constant for the group R in compounds of the form RCOOC$_2$H$_5$.

peaks are observed for ethyl and ethyl trichloroacetate and for ethyl formate, in which compounds this isomerism is not possible, is further evidence that this is the case. It can be argued further that where isomerism does occur and causes a splitting of the carbonyl band, the high frequency peak is due to the *cis* isomer and the low frequency peak is due to the *gauche* form.[12] (The term *cis* is here taken to mean *cis* to the carbonyl.) That this is the case can be seen from consideration of structures I and II. X and Y here represent either hydrogen or some other atom such as chlorine, fluorine, etc., as appropriate.

I   II
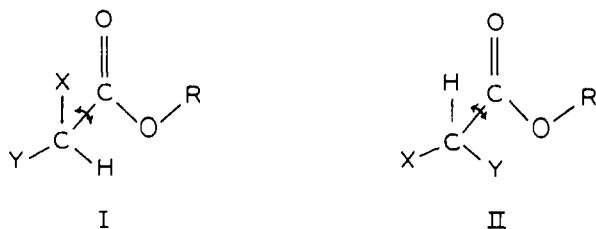
When X is in the *cis* position, the dipole represented by the C–X bond is in proximity to and parallel to the ester group dipole. Resonance in the ester group, which leads to a larger group dipole, will presumably be inhibited because of the electrostatic repulsion between the dipoles. Another way of arriving at the same conclusion would be to consider the van der Waals repulsion between X and the carbonyl oxygen. This repulsion of nonbonding electrons will certainly increase with increased negative character of the oxygen, so that the resonance form which possesses a formal negative charge on the oxygen will be inhibited. It follows from either point of view that the *cis* isomer will possess the higher carbonyl frequency and lower carbonyl intensity. The latter conclusion follows in turn from the fact that the carbonyl intensity increases regularly with resonance energy.[13]

It is interesting to note that the carbonyl band is split in all instances where rotational isomerism is possible, with the sole exception of ethyl cyano-

(12) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 4292 (1957).
(13) G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

acetate. The carbonyl absorption for this compound occurs at a frequency, which, on comparison with the bands for the monochloro, dichloro and difluoro compounds, makes it likely that the stable isomer is the *gauche*. In order to ensure that this is the case, the dipole moment was determined in benzene solution at 24.0°. The value of 3.04 Debye which was obtained agrees with that calculated for the *gauche* isomer when the dihedral angle between C—C≡N and C=O is about 120°.

In the absence of a steric effect the group R would be expected to affect the carbonyl intensity in a regular way, the more electronegative groups producing the lower intensity. In Fig. 1 the carbonyl intensity in carbon tetrachloride is plotted *vs.* the polar substituent constant, σ^*. It is readily seen that there is no regular relationship, except that for the three compounds which are essentially free of a bulky *cis* group, the relationship is roughly linear. Although this line cannot be defined with very great precision, when it is used in connection with the intensity results obtained for the other compounds, some interesting conclusions can be drawn. The arguments and conclusions presented below are not critically dependent on the exact location or slope of the line.

The value of intensity corresponding to a certain value of σ^* as defined by the line may be thought of as the intensity value which a substituent with that value of σ^* would produce if it exerted no direct steric effect on the carbonyl. This value of intensity, which represents the polar effect of the group R. corresponds to the intensity of the *gauche* isomer for R groups such as monochloromethyl, dichloromethyl, etc. It is listed in the first column of Table II as A_p. The only information obtainable from the spectrum as to the distribution of iso-

TABLE II
CARBONYL INTENSITIES CORRESPONDING TO THE *cis* ISOMER, A_c, AND THE *gauche* ISOMER, A_p

Group	A_p	n_c	A_c	ΔA
C$_2$H$_5$OCH$_2$	3.36	0.70	2.77	0.59
BrCH$_2$	3.27	0.35	2.00	1.27
ClCH$_2$	3.26	0.54	2.50	0.76
Cl$_2$CH	3.12	0.54	2.54	0.58
Cl$_3$C	3.00	1.00	2.55	0.45
F$_2$CH	3.10	0.63	2.75	0.35

mers, when both are present, is the ratio of the optical densities for the two maxima. If the band shapes for the two isomers are the same, the relative values of optical density should be a measure of the fraction of the total band area contributed by each isomer. Because of the uncertainties in resolving the band shape into the sum of two bands it is not possible to say with certainty that the band widths of the individual bands are the same, but they appear to be so.[14] If it is assumed that they are, then the fraction of the band area due to the *gauche* isomer is $\alpha_g/(\alpha_g + \alpha_c)$. The band area for the *gauche* isomer divided by cl gives the apparent value of intensity for this isomer. This

(14) The band widths for ethyl acetate, ethyl trichloroacetate and ethyl cyanoacetate are 16, 16 and 19 cm.$^{-1}$, respectively, indicating that the presence of a *cis* group does not significantly affect the band width.

value divided by A_p (Table II) represents the fraction of *gauche* isomer present, n_g. $(1 - n_g)$ then gives the fraction of *cis* isomer, n_c, listed in the second column of Table II. The band area for the *cis* isomer divided by *cl* gives the apparent value of intensity for this isomer. This divided by n_c yields the intensity for the *cis* isomer, A_c, listed in the third column of Table II.

The above treatment of the intensity results produces two quantities which are of interest. The first of these is the fraction of *cis* isomer, n_c. It is apparent that there is a direct relationship between this value and the size of the atom or group X attached to the methyl carbon. This is a rather interesting result, because it is not one which could have been predicted on the basis of current knowledge of isomer distribution. The relative stabilities of what are here designated as *cis* and *gauche* isomers is considered to be determined by two factors: the electrostatic effects arising from dipole-dipole interactions and the steric repulsive effect between the group X and the alkoxy oxygen.[10,11] It is generally recognized that in liquid media the more polar *cis* form is relatively more stable than it is in the vapor state, because of dipole-dipole or dipole-induced dipole interactions. In the present work it is clear that the compounds for which the *cis* form is more polar are the more stable in the *cis* configuration. However, since these are also the compounds with the smallest groups X, it is also possible that the van der Waals repulsive force between X and the carbonyl oxygen is a determining factor,[15] although this interaction has in the past been considered unimportant.[11] One bit of evidence which bears on this point is that the monocyano compound, although it would be very polar in the *cis* configuration, nevertheless exists entirely

in the *gauche* arrangement, so that polarity alone cannot be the determining factor.

The second quantity which bears consideration is the difference in intensity between the *cis* and *gauche* isomers for each compound, listed in the last column of Table II. This difference varies in a rough way with the size of the group X; the largest, bromine, produces the largest difference. Now if dipole-dipole interactions were responsible for the lower intensity of the *cis* isomer by virtue of their ability to inhibit resonance, as discussed earlier, the difference should be largest for fluorine and not for bromine, since the C–F bond undoubtedly possesses a larger moment than the C–Br bond. The fact that the size of the group seems to be the controlling factor strongly indicates that van der Waals repulsions are responsible for the intensity difference. These latter would surely be larger for the larger groups.

It seems quite likely that the van der Waals forces are also responsible for at least some of the difference in frequency between the *cis* and *gauche* isomer (Table I). The frequency difference does not appear to parallel the polarity of the C–X bond as it should if dipolar interactions were the major factor.[12]

A word might be said on the effect of solvent. First, it is apparent that a solvent as polar as acetonitrile nevertheless does not have a pronounced effect on the intensity; on the other hand, a hydrogen-bonding solvent such as chloroform does cause an increased intensity as a result of specific interaction with the carbonyl. The increased proportion of *cis* isomer in the more polar solvents is in accord with the results obtained by others.[11,12] The more polar *cis* form should be relatively more stable in di-polar solvents because of dipole-dipole interactions.

URBANA, ILLINOIS

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The Infrared Spectra of Dimeric and Crystalline Formic Acid

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The infrared spectra of gaseous $(HCOOH)_2$, $(HCOOD)_2$, $(DCOOH)_2$ and $(DCOOD)_2$ have been studied in the range 3800 to 625 cm.$^{-1}$. In addition the spectrum of $(HCOOH)_2$ was scanned between 600 and 150 cm.$^{-1}$; a strong band was found at 238 cm.$^{-1}$ with probably a second band at 160 cm.$^{-1}$. The infrared spectra of crystalline formic acid and its deutero forms have been measured. In the spectrum of crystalline HCOOH the center of the O–H...O stretching absorption is shifted 400 cm.$^{-1}$ toward lower frequency relative to its position in the gas phase dimer spectrum. Large crystal splittings were observed in the spectra of the solids. Small temperature dependent band shifts have been observed in the range 20–220°K. An assignment is proposed for the infrared active frequencies of all species. It is based upon an approximate application of the product rule together with the monomer assignment previously given.

Formic acid molecules hydrogen bond into two well characterized configurations, a cyclic dimer in the gas phase and a long chain polymer in the crystalline phase. We have extended our infrared study of the monomer[1] to these polymeric states. This system is advantageous for study since three deuterated derivatives of formic acid can be made easily. By comparing the infrared spectra for the monomer, dimer and crystal for

each of the isotopic species, one can obtain a detailed understanding of both the vibrational assignment and the hydrogen bonding effects.

The spectra of the dimeric acids have all been studied previously,[2-4] but the limited resolution available at that time plus the lack of understanding of the monomer assignment precluded detailed

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