

## CONFORMATION AND ELECTRONIC STRUCTURE OF AROMATIC CHLOROFORMATES

Otto EXNER and Pavel FIEDLER

*Institute of Organic Chemistry and Biochemistry,  
Czechoslovak Academy of Sciences, 166 10 Prague 6, Czechoslovakia*

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Aromatic chloroformates *Ib–Ie* were shown to exist in the *ap* conformation, in agreement with aliphatic chloroformates, *i.e.* the alkyl group is situated *cis* to the carbonyl oxygen atom as it is the case in all esters. While 4-nitrophenyl chloroformate (*Ie*) is in this conformation in crystal, in solution at most several tenths of percent of the *sp* conformation may be populated at room temperature and in nonpolar solvents only. A new analysis of dipole moments explained the previous puzzling results and demonstrated the impossibility to determine the conformation by this single method, in consequence of the strong interaction of adjoining bonds. If, however, the *ap* conformation is once proven, the dipole moments reveal some features of the electron distribution on the functional group, characterized by the enhanced polarity of the C—Cl bond and reduced polarity of the C=O bond. This is in agreement with the observed bond lengths and angles.

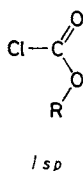
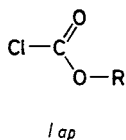
Conformation of chloroformates was studied many times with controversial results<sup>1</sup>, either the antiperiplanar<sup>2–7</sup> conformation (*I ap*) — possibly not exactly planar<sup>8,9</sup> — being preferred, or the synperiplanar<sup>10,11</sup> (*I sp*), or an equilibrium of both<sup>12,13</sup>. As far as aliphatic derivatives are concerned, a microwave study<sup>2</sup> of methyl chloroformate (*Ia ap*) may be considered as the definite solution of the problem, disproving previous claims based on dipole moments<sup>10,12</sup> and on IR and <sup>1</sup>H NMR spectra<sup>13</sup>. The conformation *I ap* is thus the same as that of common carboxylic acid esters<sup>1,14</sup> (*II sp*)\*. On the other hand, only the *sp* conformation was found for aromatic derivatives on the basis of dipole moments<sup>10,11</sup> of *Ib* and of its derivatives<sup>11</sup> *Ic–Ie*.

This evidence<sup>11</sup> from dipole moments could be held as more conclusive than in the case of aliphatic derivatives since use was made of polar substituents in *Id* and *Ie*. Although the original discussion<sup>11</sup> was not quite correct, our reinterpretation in terms of the well-tried graphical method<sup>15</sup> yielded the same result. Since opposite conformations of aliphatic and aromatic chloroformates seem *a priori* rather improbable, the latter compounds deserve a reexamination.

Recently an X-ray analysis<sup>16</sup> of 4-nitrophenyl chloroformate (*Ie ap*) confirmed the *ap* conformation even for an aromatic derivative in the crystalline state. In this

\* Note that analogous conformations of *I* and *II* are denoted with different symbols, *ap* and *sp*, respectively.

communication we present evidence from IR spectroscopy that the prevailing conformation of the latter compound in solution is the same as in crystal. Based on these results a reinterpretation of dipole moments of aromatic chloroformates *Ib–Ie* is given in terms of the conjugation within the functional group.



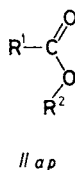
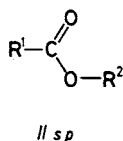
*Ia*, R = CH<sub>3</sub>

*Ib*, R = C<sub>6</sub>H<sub>5</sub>

*Ic*, R = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>

*Id*, R = 4-ClC<sub>6</sub>H<sub>4</sub>

*Ie*, R = 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>



## RESULTS AND DISCUSSION

The X-ray analysis<sup>16</sup> of 4-nitrophenyl chloroformate (*Ie ap*) will be published in detail elsewhere. In Fig. 1 some salient features of the structure are reproduced. The angles within the aromatic ring conform to the general picture for benzene derivatives as given by Domenicano and coworkers<sup>17</sup>, they correspond to the presence of two electron attracting substituents. The bond lengths and angles within the ester group differ from the mean values<sup>14</sup> for simple esters and will be discussed later in connection with the dipole moments. Most important for the present discussion is the *ap* conformation at the C—O bond. The deviation expressed by the dihedral angle C—O—C=O, equal to 5°, is easily understood in terms of crystal forces.

With this results in mind, we are able to proceed to the conformation in solution. Comparing the IR spectra of *Ie* in the crystalline state and in tetrachloromethane or acetonitrile solutions (Table I), we have found no additional bands in the latter, except possibly a weak band at 1324 cm<sup>-1</sup> in tetrachloromethane. Hence we believe that in solutions the same conformation prevails as has been found in crystal; a minor conformation, if present, could be populated to say 5% or less.

TABLE I  
The observed vibrational bands of 4-nitrophenyl chloroformate (in  $\text{cm}^{-1}$ )<sup>a</sup>

Solid in KBr <sup>b</sup>	Solution in		Assignment <sup>c</sup>
	CH <sub>3</sub> CN	CCl <sub>4</sub>	
3 523 w	—	—	—
3 120 m	3 119 w	3 118 w	20a
3 095 w	—	—	—
3 079 wm	3 085 w	3 088 w	2
3 056 vw	<i>d</i>	3 056 vw	20b
2 861 w	2 870 vw	2 870 vw	—
2 222 w	—	—	—
1 993 w	1 995 vw	1 992 vw	—
1 927 w	1 924 w	1 914 vw	—
1 782 vs	1 793 vs	1 793 vs	$\nu(\text{C}=\text{O})$
1 761 vs	1 768 sh	1 760 sh	—
—	1 755 sh	1 748 sh	—
1 728 m	—	—	—
1 698 w	—	—	—
1 623 s	1 621 m	1 620 m	8a
1 590 s	1 592 m	1 593 m	8b
1 530 vs	1 534 vs	1 535 vs	$\nu_{\text{as}}(\text{NO})_2$
1 487 vs	1 490 m	1 490 s	19a
1 466 w	<i>d</i>	—	—
1 428 w	<i>d</i>	—	—
1 370 m	<i>d</i>	1 361 sh	—
1 348 vs	1 351 s	1 347 s	$\nu_{\text{s}}(\text{NO}_2)$
—	—	1 324 w	—
1 315 m	1 316 w	1 314 w	14
1 297 w	—	—	—
1 285 m	1 289 w	1 288 w	3
1 265 m	—	—	13
1 222 m	1 228 w	1 217 m	—
1 192 vs	1 194 vs	1 195 vs	$\nu_{\text{as}}(\text{COC})$
1 163 vs	1 162 s	1 160 s	9a
1 122 vs	1 120 vs	1 114 vs	7a
1 108 vs	1 109 vs	1 101 vs	18b
1 096 sh	—	—	—
1 012 m	1 014 w	1 014 m	18a
974 w	—	—	17a
958 wm	961 vw	955 w	5
891 vs	894 m	888 m	$\nu_{\text{s}}(\text{COC})?$
863 s	863 m	861 m	$\beta_{\text{s}}(\text{NO}_2)$
829 s	833 m	829 m	17b
803 s	803 w	<i>d</i>	$\nu(\text{CCl})^e$

TABLE I  
 (Continued)

Solid in KBr <sup>b</sup>	Solution in		Assignment <sup>c</sup>
	CH <sub>3</sub> CN	CCl <sub>4</sub>	
756 w	—	—	—
740 vs	747 m	<i>d</i>	$\gamma_s(\text{NO}_2)$
685 m	685 w	681 w	$\gamma(\text{OCCl}) + 4$
675 m	675 w	674 w	12
627 w	627 vw	628 w	6b
529 w	536 vw	528 sh	$\beta_{as}(\text{NO}_2)$
504 m	506 w	505 w	16b
480 w	480 vw	—	$\beta(\text{OCO})^e$
415 m	417 w	417 w	9b
405 sh	—	—	—
327 w	<i>d</i>	<i>d</i>	—

<sup>a</sup> Unassigned very weak bands have been omitted; <sup>b</sup> the wavenumbers of very strong bands were taken from the spectrum of another KBr pellet with lower concentration of compound; <sup>c</sup> tentative assignment was made according to assignments of 4-nitrophenyl acetate<sup>18</sup>, methyl chloroformate and [2H<sub>3</sub>]methyl chloroformate<sup>6</sup>, and ethyl chloroformate<sup>7</sup>. Numbers correspond to normal vibrations of benzene according to Wilson<sup>19</sup>; <sup>d</sup> solvent or cell absorption; <sup>e</sup> preferred is the assignment by Katon and Griffin<sup>6</sup>.

We investigated in more detail the 1750–1850 cm<sup>-1</sup> region since multiple carbonyl bands found in some chloroformates (not in phenyl chloroformate) were attributed to a conformational equilibrium<sup>13</sup>. We followed the dependence on solvent

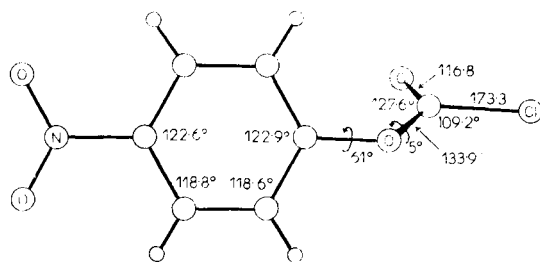


FIG. 1

Most important geometrical parameters of the structure of 4-nitrophenyl chloroformate (*Ie ap*) according to the X-ray analysis<sup>16</sup>. Bond lengths in pm

polarity in seven solvents (Table II). In nonpolar solutions the carbonyl band at  $1\,796\text{ cm}^{-1}$  is slightly asymmetric and a weak satellite appears at  $1\,815\text{ cm}^{-1}$  (Fig. 2). In polar solvents the main band is nearly symmetric, the named satellite disappears, but two others are found on the other side, near to  $1\,765$  and  $1\,752\text{ cm}^{-1}$ . The intensity of these bands does not increase with solvent polarity but changes in an irregular manner. The temperature dependence of the spectrum in decahydronaphthalene (Fig. 2) reveals a slight but regular increase of the minor band. Its integrated intensity, obtained by computer separation, reaches ultimately 1.5% of the intensity of the main band (at  $139^\circ\text{C}$ ). If this band should be assigned to a minor conformer, the latter would have a smaller dipole moment than the main conformer (according to the solvent dependence), while its C=O double bond itself should be less polarized, *i.e.* with a higher bond order (according to the position of the C=O band). Both would agree with the *sp* conformation of *Ie*. Note, however, that the equilibrium concentration of this conformer would be only some 0.2% at room temperature and this slight population prevents its proof by dipole moments or its detailed investigation by other methods. In sulfolane solution no temperature dependence was observed which could be attributed to a conformational equilibrium. The intensities both of the main band and of the two satellites decrease regularly with temperature, while their half-widths increase. Most probably the latter bands arise from Fermi resonance. We conclude that the *ap* conformation of *Ie*, found in crystal, persists even in solution. The *sp* conformer could be present only in nonpolar solvents and at elevated temperatures, in any case in minute concentrations, irrelevant for further conclusions.

In a similar way as *Ie* we also reinvestigated methyl chloroformate (*Ia*) which was claimed by Oki and Nakanishi<sup>13</sup> to consist of the conformers *ap* and *sp*, the latter

TABLE II  
Solvent dependence of infrared spectra of 4-nitrophenyl chloroformate in the carbonyl region<sup>a</sup>

Solvent	Band 1		Band 2		Band 3		Band 4	
Hexane	1 817.6	22	1 798.0	11 391	—	—	—	—
Decahydronaphthalene <sup>b</sup>	1 815.4	22	1 795.8	10 422	—	—	—	—
Tetrachloromethane	—	—	1 793.8	13 283	—	—	—	—
( <i>Z</i> )-1,2-Dichloroethene	—	—	1 790.9	16 323	—	—	1 753.9	1 145
Acetonitrile	—	—	1 793.0	13 589	1 766.8	1 187	1 752.7	500
Chloroacetonitrile	—	—	1 789.6	14 969	1 764.7	1 555	1 753.6	247
Sulfolane	—	—	1 790.0	12 341	1 764.0	387	1 751.4	321

<sup>a</sup> Results of computer separation of overlapping bands: wavenumbers ( $\text{cm}^{-1}$ ) and integrated absorption intensities ( $\text{cm}^{-2}\text{ l mol}^{-1}$ ); <sup>b</sup> 53% of the *trans* isomer.

prevailing. In contradistinction to these authors<sup>13</sup> we calculated integrated absorption intensities by computer resolution of the carbonyl band and followed it in four solvents and at variable temperature. While the resulting wavenumbers (for instance 1 774.7 and 1 786.9  $\text{cm}^{-1}$  in tetrachloromethane) agreed reasonably with ref.<sup>13</sup>, our ratio of integrated absorption intensities was quite different from the ratio of molar absorption coefficients<sup>13</sup>. Although the changes with solvent polarity could be still understood in terms of an conformational equilibrium, the temperature dependence in decahydronaphthalene or nitromethane solutions was incompatible with this interpretation, revealing only a decrease of the absorption intensity of both bands, accompanied by an increase of the absorption half-width. Hence the origin of the second band is again to be sought in the Fermi resonance rather than in a second conformer of *Ia*. Note that a thorough IR study<sup>6</sup> of *Ia* did not reveal any indication of another rotamer, and in the case of ethyl chloroformate even the claimed occurrence<sup>13</sup> of a doubled carbonyl band was not confirmed<sup>7</sup>. This example shows that it may be hazardous to infer the presence of conformers from doubled IR maxima without computer resolution and without investigating at least the temperature dependence and solvent dependence in several solvents. This was the shortcoming of several other papers of Oki and Nakanishi<sup>20</sup> which are also at variance with the results obtained by other methods<sup>21-23</sup>. We are thus of the opinion that an essential part of these results<sup>13,20</sup> is in error.

When the conformation of chloroformates is unambiguously established, their dipole moments have to be reinterpreted in terms of conjugation and mutual induction of adjoining bonds. The dipole moment of phenyl chloroformate (*Ib*) was measured several times with accordant results<sup>8,10,11</sup>. Since it does not differ too much from those of aliphatic chlorocarbonates, the conformation inferred was also the same<sup>10-12</sup>, mostly *sp*. However, the values calculated for the two conformations from bond moments are not sufficiently different from each other, e.g.<sup>10</sup> 5.3 and 6.7, or<sup>11</sup> 5.3 and 7.4 (all dipole moments in  $10^{-30}$  Cm) for the *ap* and *sp* conformation, respectively. In addition, the agreement with experiment is rather bad even for the *sp* conformation. The whole procedure was criticized<sup>8</sup> with regard to the non-constancy of bond moments and possible mutual polarization of neighbouring bonds but an agreement of the experiment with *ap* conformation was reached only after introducing quite unusual, *ad hoc* modified bond moments<sup>8</sup>. Measurements on *para*-substituted derivatives *Ic*–*Ie*, offer the possibility to obtain more definite results which was not exploited by the authors<sup>11</sup>. We processed the experimental dipole moments<sup>11</sup> in two ways. According to the standard procedure<sup>15</sup> we calculated the expected dipole moments for the two conformations using bond angles from the X-ray data and standard bond moments<sup>24</sup> (for the  $\text{NO}_2$  group the value of 14.7, accounting for the conjugation). The calculated values were plotted as  $\mu^2$  in a graph, the unsubstituted compound *Ib* on the *x*-axis, the substituted ones, *Id* and *Ie*, on the *y*-axis (Fig. 3). Comparison with the experimental point (the hatched circle, representing

the combined inaccuracy of experiment and calculations) reveals that neither conformation squares with the experiment, although the deviation is smaller for *sp*.

In order to analyze the said deviations we used another graphical representation (Fig. 4). First the direction of the experimental dipole moment was determined from the values measured on the substituted and unsubstituted compound, and from the known moment of the substituent<sup>24</sup>. This procedure means to construe a triangle given its three sides. By repeating for the substituents Cl, NO<sub>2</sub>, and CH<sub>3</sub> a good agreement is obtained. The resulting mean dipole moment for *Ib* is 7.9 at an angle of 33° to the C(1)—O bond (heavy arrow). This vector does not coincide with calculations for either conformation (light arrows), the agreement being still better for the incorrect *sp* conformation. Within the framework of the bond moment scheme, the observed discrepancy can be formally described by an enhanced C—Cl bond moment and possibly slightly reduced C=O and C(O)—O bond moments. These deviations cannot be understood either in terms of inductive polarization or of conjugation within the functional group. The mutual polarization of adjoining dipoles<sup>25</sup> (as *e.g.* in dichloromethane) would reduce both the apparent C—Cl and C=O bond moments, contrary to the observation. The conjugation within the functional group is usually expressed by the mesomeric formulae *IIIa*—*c*. While the mesomerism *IIIa* ↔ *IIIb* is common

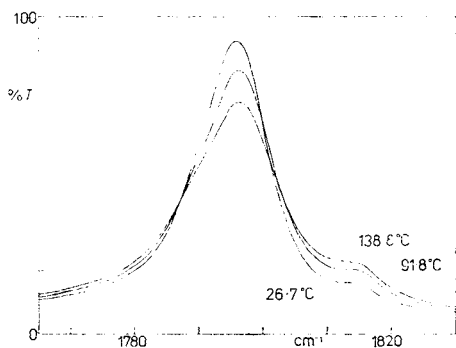


FIG. 2

The carbonyl region of the IR spectrum of *Ie* in decahydronaphthalene at variable temperature

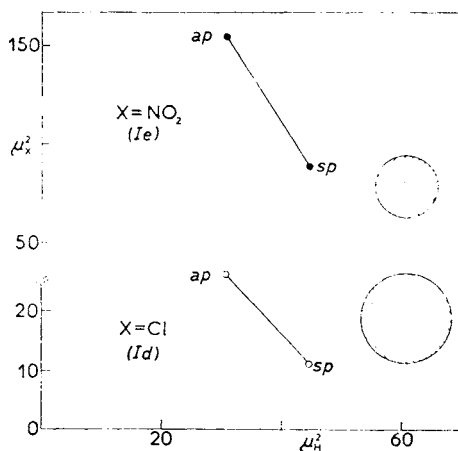
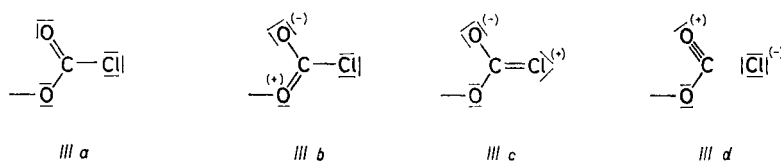


FIG. 3

Comparison of squared dipole moments of aryl chloroformates *Ib* (on the *x*-axis), with *Id* and *Ie* ( $X.C_6H_4.OOC.Cl$ , on the *y*-axis). Closed points refer to the values calculated for conformations *ap* and *sp*, respectively; hatched circles correspond to experimental values according to ref.<sup>11</sup>

to all esters, formula *IIIc* describes the  $n-\pi$  conjugation involving chlorine. Both *IIIb* and *IIIc* would predict approximately opposite effects than observed. If we want to picture this observed effect, we are forced to use the symbolic formula *III d* which shows an extended and more polar C—Cl bond, and a shortened and less polar C=O bond. Besides the dipole moments, this formula also rationalizes some of the observed bond lengths and angles (Fig. 1). Significant is particularly shortening of the C=O bond compared to the mean value in simple aromatic esters<sup>14</sup>, further the widened O—C=O angle. In both cases, formula *IIIc* would require just the opposite. As regards the C—Cl bond, its length is practically equal as in other compounds with chlorine on an  $sp^2$  carbon (*e.g.* chloroethene) and its enhanced polarity is revealed only in dipole moment values.



We searched for a similar effect in acyl chlorides as simpler model compounds. The experimental dipole moments<sup>26</sup> of benzoyl chloride and its 4-chloro, 4-bromo,

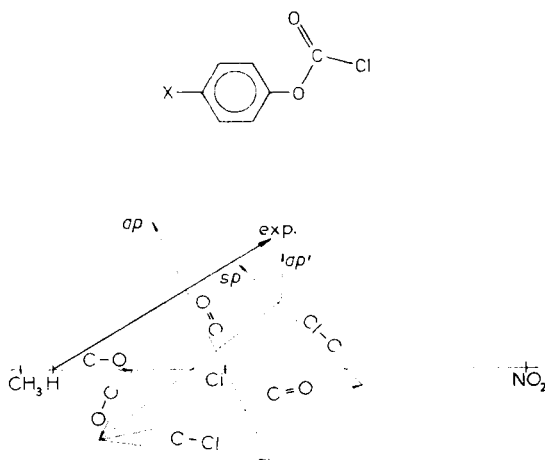


Fig. 4

Analysis of the dipole moments from Fig. 3 in terms of vectors. The direction of the dipole moment of *Ib* (heavy arrow) was determined from the experimental dipole moments of *Ib—Ie*. Light arrows represent calculations from bond moments for the two conformations, *ap* and *sp*, and with different assumptions, respectively (points *ap*, *sp*, and *ap'*)



and 4-nitro derivatives were plotted in the same way as in Fig. 4. An empirical correction of 4.7 for the conjugation with the benzene nucleus was subtracted as estimated from the comparison to the dipole moment of acetyl chloride<sup>26</sup>. The resulting group moment of the group  $-\text{C}(\text{O})\text{Cl}$  is 7.2 at an angle either  $+26^\circ$  or  $-26^\circ$  to the  $\text{C}-\text{C}$  bond, *i.e.* directed either toward the side of oxygen or of chlorine. The latter possibility has been plotted into Fig. 4 and complemented by a contribution of the  $\text{O}=\text{C}-\text{O}$  conjugation, not present in acyl chlorides and estimated to 1.5 (the dot-and-dash arrows, the end-point *ap'*). The agreement with the experimental values for chloroformates is not bad, considering several assumptions and estimates involved. It can be interpreted that the electron distribution in acyl chlorides and chloroformates is similar. Note that the choice of the angle  $-26^\circ$  was rather arbitrary. In fact, if the dipole moment of benzoyl chloride were directed at an angle of  $+26^\circ$  (*i.e.* toward oxygen atom), it would relatively better correspond to the vector sum of standard bond moments  $\text{C}=\text{O}$  and  $\text{C}-\text{Cl}$ . On the other hand, the former possibility, preferred by us, requires an enhanced polarity of the  $\text{C}-\text{Cl}$  bond and reduced polarity of  $\text{C}=\text{O}$ , in agreement with the bond lengths measured on acetyl chloride<sup>27</sup>.

Summarizing, the dipole moments of chloroformates are affected by interactions of adjoining bonds and can be rationalized with reference to acyl chlorides as model compounds. In this way the dipole moments can be understood but a trustworthy determination of conformation by this single approach is not feasible and would require at least a larger set of further model compounds.

The conformation *I ap* was found for aromatic as well as aliphatic chloroformates at different conditions. It corresponds to the conformation of common esters (*II sp*), the replacement of alkyl by chlorine being irrelevant in this respect. Note also several other types of esters and their analogues for which the assumed reversed conformation has been disproved<sup>1</sup>. Hence it seems that the conformation of all these compounds is controlled by an interaction of the alkoxy and carbonyl group. The electronic interactions between the three polar bonds at carbon in *I* are considerable but can be only very roughly pictured by mesomeric formulae.

## EXPERIMENTAL

4-Nitrophenyl chloroformate (*Ie*), m.p.  $82^\circ\text{C}$  (cyclohexane). The infrared spectra were recorded on a Perkin-Elmer model 580 spectrometer, with a precision of  $\pm 0.5\text{ cm}^{-1}$  in the range  $350$  to  $4000\text{ cm}^{-1}$ , in a KBr pellet and in solutions in tetrachloromethane and acetonitrile (concentration  $0.15\text{ mol l}^{-1}$ ,  $d = 0.1\text{ mm}$ ). The spectral region near to the carbonyl band was measured at a 20x expanded scale (calibration with  $\text{H}_2\text{O}$  vapour), concentration  $0.012\text{ mol l}^{-1}$  with  $d = 1\text{ mm}$  (in *n*-hexane, decahydronaphthalene, and tetrachloromethane), or  $0.15\text{ mol l}^{-1}$  with  $d = 0.1\text{ mm}$  (in (*Z*)-1,2-dichloroethene, acetonitrile, chloroacetonitrile, and sulfolane). The temperature dependence of *Ie* was investigated in the range  $26.7$ – $138.8^\circ\text{C}$  in decahydronaphthalene, or  $33.6$ – $80.4^\circ\text{C}$  in sulfolane, that of *Ia* in decahydronaphthalene between  $32$  and  $110^\circ\text{C}$ , in nitromethane between  $28$  and  $87^\circ\text{C}$  (copper-constantan thermocouple). The correction for con-

centration change with temperature was carried out using tabulated values of densities and estimating some values<sup>28</sup>. The band separation and calculation of integrated absorption intensities was accomplished on a Hewlett-Packard 9830 calculator, using a program based on Lorentz-type band shape<sup>28</sup>.

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