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Infrared spectroscopic studies of the conformation in ethyl α -haloacetates in the vapor, liquid and solid phases

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ABSTRACT

Infrared spectra of ethyl α -fluoroacetate, ethyl α -chloroacetate, ethyl α -bromoacetate and ethyl α iodoacetate have been measured in the solid, liquid and vapor phases in the region 4000-200 cm⁻¹. Vibrational frequency assignment of the observed bands to the appropriate modes of vibration was made. Calculations at DFT B3LYP/6-311+G** level, Job: conformer distribution, using Spartan program '08, release 132 was made to determine which conformers exist in which molecule. The results indicated that the first compound exists as an equilibrium mixture of cis and trans conformers and the other three compounds exist as equilibrium mixtures of cis and gauche conformers. Enthalpy differences between the conformers have been determined experimentally for each compound and for every phase. The values indicated that the trans of the first compound is more stable in the vapor phase, while the cis is the more stable in both the liquid and solid phases. In the other three compounds the gauche is more stable in the vapor and liquid phases, while the cis conformer is the more stable in the solid phase for each of the second and third compound, except for ethyl α -iodoacetate, the gauche conformer is the more stable over the three phases. Molar energy of activation Ea and the pseudo-thermodynamic parameters of activation ΔH^{\ddagger} , ΔS^{\ddagger} and ΔG^{\ddagger} were determined in the solid phase by applying Arrhenius equation; using bands arising from single conformers. The respective E_a values of these compounds are 5.1 ± 0.4 , 6.7 ± 0.1 , 7.5 ± 1.3 and 12.0 ± 0.6 kJ mol⁻¹. Potential energy surface calculations were made at two levels; for ethyl α -fluoroacetate and ethyl α -chloroacetate; the calculations were established at DFT B3LYP/6-311+G^{**} level and for ethyl α -bromoacetate and ethyl α -iodoacetate at DFT B3LYP/6-311G^{*} level. The results showed no potential energy minimum exists for the gauche conformer in ethyl α -fluoroacetate. © 2010 Elsevier B.V. All rights reserved.

1. Introduction

The early investigations of conformations in esters were on ethyl α -chloroacetate and ethyl α -bromoacetate using infrared spectroscopy [1,2]. These works reported presence of cis and gauche conformers with X–C–C=O dihedral angles $\Phi = 0^{\circ}$ and 120° respectively, the cis being more stable than the gauche. The results suggest that the repulsion between the halogen and ether oxygen is stronger than that between the halogen and the carbonyl oxygen. Later work on infrared intensity of couples of C=O bands at different temperatures on ethyl α -fluoroacetate in the vapor phase [3] reported presence of trans and gauche conformers. While, two groups of work on unsubstituted acetates suggest presence of cis and trans, with the cis being the more stable conformer [4,5].

A part from the above studies a ^{13}C NMR work on $\alpha\text{-}$ monosubstituted methyl acetates (substituent=F, Cl, Br, and I)

[6] reports presence of cis and gauche conformation. On the other hand, NMR works on rotational isomerism of methyl α -fluoroacetate in the vapor phase and in various solvents suggest presence of cis and trans conformers [7]. While a Raman and infrared work on the same compound in the vapor and liquid phase together with ab initio calculations reports trans and gauche conformation [8]. An ¹H NMR and ¹³C NMR work on α -monosubstituted ethyl acetates (substituent = F, Cl, Br, and I) together with relative energy calculations carried out at B3LYP/6-31G level for the first three compounds and at B3LYP/3-21 G level for ethyl α -iodoacetate suggest presence of cis and trans conformers in ethyl α -fluoroacetate with the trans being the more stable and cis and gauche in each of ethyl α -chloroacetate, ethyl α -bromoacetate and ethyl α -iodoacetate with the gauche being the more stable conformer [9].

These results raise interesting questions regarding the number of conformers 2^n that would exist, where *n* is the number of asymmetric centers in the molecule, which conformers exist in which molecule, the conformation preferences and the interactions responsible for the presence of cis-trans or cis-gauche or transgauche equilibriums. To explore these further, we have undertaken

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Scheme I. Some of the possible conformers of ethyl α -haloacetate (X = F, Cl, Br, and I).

infrared studies of ethyl α -fluoroacetate, ethyl α -chloroacetate, ethyl α -bromoacetate and ethyl α -iodoacetate in the solid, liquid and vapor phases. It was felt that by studying such a series as this can one hope to make a reasonable account for the factors that determine stability of the conformers for the members of the series and to measure their enthalpy differences and molar energy of activation of the interconverting conformers. To the best of our knowledge, no previous infrared work has been published on these compounds in the same program as ours.

2. Experimental

Ethyl α -fluoroacetate and ethyl α -chloroacetate are commercial liquids furnished by Fluka Buchs S.G. of stated purity 98%. They were repurified by drying over magnesium sulfate for 2 days. After filtrations, fractional distillation was carried out at normal conditions. Middle portion was collected for each compound at their b.p. 117 °C and 143.5 °C, respectively. Ethyl α -bromoacetate was prepared by conventional method [10] through esterification of bromoacetic acid by mixing with absolute ethyl alcohol. The dry product was purified by fractional distillation at reduced pressure [6 mm Hg]. Middle portion was collected at its b.p. 58 °C. Ethyl α bromoacetate was prepared by displacement reaction between ethyl α -bromoacetate and potassium iodide in acetone base at room temperature [11]. After drying, fractional distillation was carried out at reduced pressure [12 mm Hg]. Middle portion was collected at its b.p. 73 °C.

The infrared spectra of these compounds were recorded on Perkin-Elmer599B Infrared Spectrophotometer in the region 4000–200 cm⁻¹ using CsI windows. Controlled variable temperature cell Specac type fitted with thermocouple wire was used in two temperature ranges 248–123 K and 298–538 K for the solid and liquid phases, respectively. It was controlled to ± 1 °C in every case. Liquid nitrogen was used for cooling. In the vapor phase, a 10 cm path length glass gas cell was used with CsI windows [Pye–Unicam] fitted with the thermocouple wire and wound by an asbestos heating tape gated to temperature controller unit type tem-1.

The spectral bands that are identified to arise from two different conformers were measured five times at each temperature. Average values of the absorbance were taken in the calculation. The IR instrument was programmed to high resolution so that to provide a spectral slit width of $1/5 \Delta v_{1/2}$, with $\Delta v_{1/2}$ being the band width at half height of the absorption [12]. It was calibrated by using a pair of bands of 1,2-dichloroethane vapor phase spectrum arising from two different conformers measured at different temperatures. It gave $\Delta H^{\circ} = 4.26 \pm 0.28$ kJ mol⁻¹ which is in good agreement with published values $\Delta H^{\circ} = 4.28$ and 4.6 kJ mol⁻¹ [13,14].

Molar energy of activation was estimated by measuring the rate constants k through tracing the growth of a band identified to arise from a single conformer in the crystalline phase. The same method of cooling and annealing was used in these measurements. While cooling the crystalline sample, the relevant band was recorded to observe its intensity changes. When no significant reduction in band intensity is observed, the sample was allowed to heat. By setting the spectrophotomer at fixed wavenumber and starting time drive program to record time in minutes; the band maximum was recorded at certain temperature. The same procedure was repeated for the subsequent measurements of intensity of this peak at higher

Table 1

Calculated parameters at level DFTB3LYP/6-311+G** of conformer distribution for the cis, gauche and trans conformations of ethyl α -halacetates.

Parameters	Ethyl α-fluoro	oacetate	Ethyl α-chlor	oacetate	Ethyl α-bromo	acetate	Ethyl α-iodoacetate		
	Cis	Trans	Cis	Gauche	Cis	Gauche	Cis	Gauche	
Energy (Hartrees)	-407.1384	-407.1386	-767.5643	-767.5646	-2881.8880	-2881.8895	-7228.0936	-7228.0972	
Relative energy (kJ/mol)	0.64	0.000	0.000	-0.74	0.000	-4.05	9.35	0.000	
Dipole moment μ (D)	3.98	1.19	3.81	2.35	3.66	2.42	3.43	2.41	
$D(X_1 - O_1 = C_1) (Å)$	2.731	3.549	3.021	3.642	3.135	3.687	3.249	3.820	
$D(X_1 - O_2)(Å)$	3.541	2.612	3.943	3.161	4.096	3.342	4.311	3.600	
$\Phi(X_1 - C_2 - C_1 = O_5)$	0.00	180.0	0.00	112.8	0.00	104.1	0.00	97.6	
$\Phi(H_1-C_2-C_1=O_5)$	120.3	58.9	120.7	128.3	59.6	166.1	119.8	18.8	
$\Theta(X_1-C_6-C_1)$	110.7	113.9	112.9	111.4	113.5	110.6	112.6	111.1	
$\Theta(C_6-C_1=O_1)$	125.4	120.6	127.0	123.5	126.9	123.2	126.9	124.1	
$\Theta(C_6-C_1-O_2)$	109.4	114.0	108.1	111.5	108.1	111.4	109.0	113.3	
$\Theta(C_1-O_2-C_3)$	116.6	116.7	117.2	116.5	117.3	116.4	115.7	116.5	
$\Theta(O_2-C_1=O_1)$	125.4	125.7	125.3	124.9	124.1	124.7	124.2	124.6	
$D(X_1 - C_6)$	1.379	1.385	1.790	1.811	1.947	1.971	2.176	2.199	
$D(H_3-C_2)$	1.093	1.093	1.089	1.085	1.088	1.085	1.088	1.084	
$D(C_6 - C_1)$	1.522	1.521	1.523	1.518	1.521	1.513	1.521	1.508	
$D(C_1=O_5)$	1.200	1.208	1.200	1.206	1.200	1.206	1.201	1.206	
$D(C_1 - O_2)$	1.346	1.331	1.347	1.338	1.348	1.340	1.348	1.343	
$D(O_2 - C_3)$	1.454	1.455	1.454	1.453	1.455	1.453	1.456	1.453	

 Φ , dihedral angle in degrees.

 Θ , tri-atomic angle in degrees.

d: bond distance (-) and D: intra-molecular distances (····) in Angstrom (Å) unit.

temperatures and times. Then absorbances at the corresponding temperature and time were determined from which rate constants have been calculated.

3. Results and discussion

The structural configuration of ethyl α -haloacetate molecule predicts at least three possible conformers [cis, gauche and trans] as depicted in Scheme I. Each conformer of the molecules in this series of compounds is expected to display 36 fundamental modes of vibration each of which should be infrared and Raman active. They are distributed as 22Aĭ +14 A["] for each of the cis and trans conformers (point group C_s). While for the gauche conformer (point group C₁) all the 36 modes are of symmetry class A. Hence, 72 distinct fundamental bands are theoretically possible for each couple of conformers. In practice, this number of bands is never found since the corresponding vibrational modes in the two conformers usually have virtually identical frequencies which result in an infrared band common to both species. Hence it is usually found that the solid phase spectrum of these molecules is simplified by loss of some bands compared with the liquid phase spectrum.

3.1. The theoretical calculations

The geometry of ethyl α -haloacetate molecule indicates that the repulsion between the halogen atom and ether oxygen in the trans position is stronger than that between the halogen and the carbonyl oxygen in the cis position, thus suggesting preference of cis or gauche conformation over the trans [see Table 1]. The theoretical calculations using Spartan '08, release 132 a commercial program at DFT B3LYP/6-311+G** level, Job: conformer distribution; reveal that there are two stable conformers in each compound of this series of molecules. For ethyl α-fluoroacetate they are cis and trans, with the trans being the more stable conformer, while for each of ethyl α -chloroacetate, ethyl α -bromoacetate and ethyl α -iodoacetate they are cis and gauche. The results of calculations are set out in Table 1. They infer that the energy difference value for ethyl α -iodoacetate $\Delta E = -9.45$ kJ mol⁻¹ is in good agreement with the experimental value $\Delta H^{\circ} = -9.1 \pm 1.7 \, \text{kJ} \, \text{mol}^{-1}$ of the vapor phase [see Table 5]. The corresponding value for ethyl α -bromoacetate $\Delta E = -3.94$ kJ mol⁻¹ is lower than the experimental value $\Delta H^{\circ} = -6.7 \pm 2.5 \text{ kJ mol}^{-1}$ of the vapor phase. The values for the fluoro- and chloro-compounds are still lower. They are $\Delta E = -0.5$ and -0.79 kJ mol⁻¹ compared with the experimental values of the vapor phase ΔH° = -3.8 ± 1.7 and -4.2 ± 1.7 kJ mol⁻¹ of fluoro and chloro compounds, respectively. However, the values of Table 1 are much better than those of the basis sets RHF/6-31 G^{*}, RHF/6-311G*, DFT B3LYP/6-31G*and DFT B3LYP/6-311++G**. The result for the fluoro-compound has a support in [9] in that it suggests presence of cis and trans conformers in ethyl α -fluoroacetate [see Table 1 of ref. [9]].

The potential energy surface calculations were carried out at two levels; one for ethyl α -fluoroacetate and ethyl α -chloroacetate the calculations were performed at level DFT B3LYP/6-311+G** and the other for ethyl α -bromoacetate and ethyl α -iodoacetate at DFT B3LYP/6-311G* level. Fig. 1 shows the potential energy surfaces of ethyl α -haloacetates where plots of the relative energy (kJ mol⁻¹) against the constraint dihedral angle Φ (X–C–C=O) were made. Both Table 1 and Fig. 1 have established existence of the first compound as equilibrium mixture of cis (Φ = 0°) and trans (Φ = 180°) conformers with slight predominance of the trans with no potential energy minimum for the gauche conformer [see Fig. 1a]. This result has a support in Ref. [7], in that methyl α -fluoroacetate has no potential energy minimum.



Fig. 1. Potential energy profile showing plots of relative energy $(kJ \text{ mol}^{-1})$ against the constraint dihedral angle (Φ) for ethyl α -haloacetate: (a) ethyl α -fluoroacetate, (b) ethyl α -chloroacetate, (c) ethyl α -bromoacetate, and (d) ethyl α - iodoacetate.

The results of Table 1 infer that the dihedral angle Φ (X–C–C=O) of the predominant conformer decreases as the electronegativity of the halogen atom is decreased, the values are: 180°, 112.8°, 104.1° and 97.6° for the fluoro, chloro, bromo- and iodo-compounds, respectively. The energy difference between conformers of these compounds increases as the atomic mass of the halogen atom is increased, the order of which is as follows; F<Cl<Br<I. It can be seen from Table 1 also that, geometry of the molecules changes with conformational interconversion and change of substituents. The bond distances of each couple of conformers increases as the electronegativity of the halogen is decreased. Further, we have found that the frequency of C=O stretching bands of the two stable conformers is linearly related to the dihedral angle Φ (X–C–C=O). The plot of the experimental wavenumbers of C=O stretching bands of the conformers of these compounds in the vapor phase against the calculated dihedral angles $\Phi(X-C-C=0)$ gave a good straight line as shown in Fig. 2. This plot can foretell which bands belong to which conformers.

Stability preference of the gauche conformer over the cis in the last three compounds may be ascribed to three factors. First, the molecular orbital interactions of the type $\pi^*_{C=0} \rightarrow \sigma^*_{X-C}$ and second the hyperconjugative effect of the type $\sigma_{X-C} \rightarrow \pi^*_{C=0}$ [15,16]. The experimental evidence for the latter effect can be seen from the decreasing absorptivity ratio D_c/D_g of the carbonyl bands arising from cis and gauche conformers of the last three compounds; the approximate values are: 0.77, 0.68 and 0.54 for the chloro-, bromo- and iodo- compounds, respectively. These values indicate increasing stability of the gauche conformer with the increase of the C–X bond polarizability. The correlation, may be interpreted in terms of interaction between unperturbed σ_{C-X} and $\pi^*_{C=0}$ orbitals



Fig. 2. Plot of the wavenumbers (cm⁻¹) of the conformers against the calculated dihedral angle Φ (X–C–C=O) of ethyl α -haloacetates. F: ethyl α -fluoroacetate, CI: ethyl α -chloroacetate, Br: ethyl α -bromoroacetate and I: ethyl α -iodoacetate.

within the molecule in a second-order perturbation equation as a result of considerable energy gap between them [16,17]. The values of C–X bond polarizability are: C–F [0.67 Å³], C–Cl bonds [2.53 Å³], C–Br [3.61 Å³] and C–I bond [5.4 Å³] [16]. Third, the intra-molecular distance X…O₂ in the gauche conformer is larger than X…O=C in the cis form [see Table 1].

3.2. The assignment

Frequency assignment of the infrared bands to the approximate modes of vibration of the trans and cis conformers of ethyl α -fluoroacetate and cis and gauche conformers of each of ethyl α -chloroacetate, ethyl α -bromoacetate and ethyl α iodoacetate are given in Table 2. They are tentative particularly with reference to the modes of vibration involving CH₃ and CH₂ groups. We have adopted in the assignment the order $v(CH_3) > v$ $(CH_2) > d(CH_2) > w(CH_3) > w(CH_2) > tw(CH_3) > tw(CH_2) > r(CH_3) >$ r(CH₂). The same order was followed with respect to the modes of vibration involving XCH₂ groups. The assignment has been built mainly on the spectral changes that have been observed between spectra of the different phases, thermal changes, and solvent effects and with taking advantage of having been made for four similar molecules and on comparisons with literature as will be mentioned later on. One can see from Table 2 that the assignments are internally consistent but since they must be to some extent arbitrary they will not be discussed in detail except for few specific points. Fig. 3 shows solid, liquid and vapor phase spectra of ethyl α -fluoroacetate as a representative figure for all spectra of the compounds of the series of molecules of the present work.

The bands which have appeared in the vapor phase spectrum and disappeared in the solid phase are: for ethyl α -fluoroacetate: 1295, 1216, 1111, 1097, and 1038 cm⁻¹; for ethyl α -chloroacetate: 1315, 1300, 1295, 1169, 1117 and 1048 cm⁻¹; for ethyl α bromoacetate: 1212, 930, and 717 cm⁻¹ with a band decreases in intensity at 1282 cm⁻¹ and for ethyl α -iodoacetate: 1337, 1209, and 1040, 1028 cm⁻¹. Thus, there is no doubt that these bands should be assigned to the trans for the first compound and to the gauche conformer for the last three compounds.

In addition, there is some bands increase in intensity and others decrease upon the shift from phase to phase in the trend: solid–liquid–vapor. For ethyl α -fluoroacetate, the ratio D_{1472}/D_{1461} takes the values: 0.46, 1.23 and 2.00; ethyl α -chloroacetate, D_{1438}/D_{1425} : 0.19, 0.58 and 1.00; ethyl α bromoacetate, D_{1416}/D_{1400} : 1.92, 1.22 and 1.00, and another ratio, D_{556}/D_{572} : 1.22, 1.50 and 2.50, and for ethyl α -iodoacetate D_{1392}/D_{1386} : 0.76, 1.00 and 1.33.The bands which increase in the vapor phase were assigned to the trans in the first compound and to the gauche for the other three compounds and those who decreased assigned to the cis with respect to the first three compounds and to the gauche with respect to the last compound. There are many other bands show increase or decrease in the absorptivity ratios which were of great help to the assignment.

3.3. The carbonyl stretching bands

The infrared spectra of the vapor phase Fig. 3c, for ethyl α fluoroacetate show two strong doublets in the region of C=O stretching mode of vibration. The first appears at 1803 and 1793 cm^{-1} and the second at 1772 and 1765 cm^{-1} . In the middle of these doublets there is a peak at 1782 cm⁻¹. Both doublets are fundamental bands with the first being resolved into R and P branches. The former has been reduced in intensity into a very weak shoulder in the liquid phase, while the second fundamental band at 1772 cm⁻¹ and its shoulder at 1765 cm⁻¹ persisted in the liquid phase [Table 2] with persistence of the middle peak in this phase and appears as a hump. The middle peak at $1782 \,\mathrm{cm}^{-1}$ may be a combination band $(923 + 865 \text{ cm}^{-1})$ deriving its intensity from Fermi resonance with the fundamental. A report on methyl αfluoroacetate confirmed that this peak is a Fermi resonance band by recording the first overtone of the carbonyl bands which appeared as two well resolved bands with no first overtone of this band [7]. However, we could not confirm that this peak is a Fermi resonance band because the first overtones of the carbonyl bands are too weak to be recognized. In the solid phase, the first doublet 1803 and 1793 cm⁻¹ has disappeared almost completely, while the band at 1772 cm⁻¹ appeared at 1752 cm⁻¹ as a very strong and thin band (Fig. 3a).

A worthwhile point to note is that, we found a linear relationship between the frequency difference of C=O stretching bands arising from the cis and gauche conformers of the chloro, bromo and iodo compounds and the corresponding calculated dihedral angle $\Phi(X-$ C-C=O). It is likely from the frequency differences measured for these compounds that a hypothetical frequency difference value between cis and gauche conformers for ethyl α -fluoroacetate can be estimated by extrapolation on the assumption that the corresponding dihedral angle Φ = 120°. Thus, the respective $\Delta \nu$ (cm⁻¹) values for these three compounds 22, 18, 17 cm⁻¹ and the corresponding Φ = 112.8°, 104.1° and 79.6° allowed extrapolation into a value of 24 cm⁻¹. Thus, by comparing this value with the experimental frequency difference $\Delta v = 31 \text{ cm}^{-1}$ between the band at 1803 and 1772 cm⁻¹, we found that the $\Delta v = 31$ cm⁻¹ is between cis and trans conformers. Thus, suggesting that the doublet (1803 and 1793 cm⁻¹) arises from the cis conformer and the second doublet at 1772 and 1765 cm^{-1} arises from the trans.

The solvent effect studies on the intensity variation of ethyl α haloacetate in various solvents, can distinguish between the more polar and less polar conformers. The plots of absorbance *D* against the dielectric constant function $(\varepsilon + 1)/(2\varepsilon + 1)$ of the solvents give rise to two lines; one for the more polar conformer and the other for the less polar one as shown in Fig. 4. The plots of the couple of carbonyl stretching bands at 1803 and 1772 cm⁻¹ of ethyl α fluoroacetate in various solvents; indicate that the first band arises from a more polar conformer and the latter arises from a less polar one. Hence, there is no doubt according to the theoretical calculations that the first doublet can be assigned to the cis conformer and the second to the trans which lend support to the above analysis.



Fig. 3. Infrared spectra of ethyl α -fluoroacetate in the: (a) solid, (b) liquid and (c) vapor phase.

Table 2

Ethvl α-fluoroacetate Ethvl α-chloroacetate Ethvl a-bromoacetate Ethvl α-iodoacetate Assignment Solid Solid Solid Solid Liquid Vapor Liquid Vapor Liquid Vapor Liquid Vapor 3006 wsh 3007 msh 3006 s 2996 m 3008 s 2996 msh 2998 msh 3015 msh 3007 m 3016 m 3001 msh 3011 msh v_{as} CH₃ (t), (g) 2995 msh 2998 msh 3001 s 2981 msh 2991 ssh 2996 msh 2996 msh 2998 ssh 3000 wsh 2981 ssh 2981 ssh 2993 wsh v_{s} CH₃ (c), (c) 2986 s 2992s 2992 s 2971s 2976mfirst 2977 s 2981ssh 2981ssh 2986 ssh 2976 ssh 2976 ssh 2986 ssh v_{as} CH₂, v_{as} XCH₂, (t), (g) 2976 wsh 2983 msh 2981 wsh 2964 s 2956 ssh 2966 ssh 2976 msh 2978 msh 2981 wsh 2961 ssh 2964 msh 2976 wsh $v_{s} XCH_{2}$ (t), (g) 2971 ssh 2976 msh 2948 wsh 2951ssh 2956 msh 2969 msh 2966 msh 2971 msh 2956 msh 2961 wsh 2963 msh v_{as} CH₂ (c), (c) 2944 wsh 2956 wsh 2971 msh 2911 wsh 2916 wsh 2921 msh 2941 msh 2941 msh 2948 wsh 2941 wsh 2941 wsh $v_{s} CH_{2}$ (c), (c) 2906 wsh 2918 wsh 2885 wsh 2881 wsh 2896 wsh 2911 wsh 2911 wsh 2918 wsh 2905 wsh 2905 wsh $v_{as} CH_2$ (t), (g) 2881 wsh 2886 wsh 2841 wsh 2852 wsh 2876 wsh 2876 wsh 2886 wsh 2882 wsh 2882 wsh $v_{s} CH_{2}$ (t), (g) 1803 wsh 1803 1793[]]wsh 1803 1793 []]v.s 1774 wsh 1794 wsh 1790 wsh 1790 wsh 1770 wsh 1793 msh 1794 vw 1782 msh 1785 vssh 1785 wsh 1765 wsh 1772 vsb 1786 ssh v C=O (c), (c) 1756 vssh 1782 ssh 1760 wsh 1760 ssh 1749 vssh 1774 s.sh 1756 vs 1782 vssh 1768 vs 1760 ssh 1765 s 1772 vs Fermi resonance band 1782 wsh 1782 wsh 1782 wsh $(923 + 865 \text{ cm}^{\Box 1})$ $\frac{1772}{1767}$ v.s1760 msh 1772]_{v.s} 1750 vs 1752 vs 1752 vssh 1738 ssh 1759 vs.sh 1757 vssh) 1752 vssh 1730 ssh 1746 vssh) 1738 vs.b 1750 vssh 1745 v.s 1735 msh 1752 msh 1732 vsb 1750 vssh v C=O(t), (q)1748 s.sh 1720 msh 1746 ssh 1745 vs 1737 ssh 1731 vssh 1742 wsh 1734 msh 1745 msh 1730 wsh 1728 msh 1720 wsh. 1721 wsh 1726 wsh 1732 wsh 1715 wsh 1718 wsh 1490 vw 1488 vw 1483 vwsh 1486}₅ 1480 1479 1472} vs 1490 msh) 1488 msh 1489 s 1485) 1490 wsh 1479 vssh 1477 vs 1489 vw 1472 w $b_{o/P} CH_2$, (t), (g) 1481 vw 1482 vw 1479 s 1478 wsh 1479 ssh 1486 wsh 1472vs 1472 vwsh 1472 vwsh 1472 vwsh 1470 wsh 1473 wsh 1472 vw 1472 wsh 1470 vs 1473 w 1468 vssh 1467 vs 1473 vs b_{I/P} CH₂, (c), (c) 1461 vwsh 1463 ssh 1463 wsh 1465 wsh 1466 wsh 1463 msh 1464 wsh 1466vssh 1468 wsh 1468 vssh 1467 vs 1468 w b_{as} CH₃, (t), (g) 1455 vwsh 1457 vw 1457 wb 1457 w 1458 msh 1458 wsh 1455 s 1456 wsh 1458 wsh 1456vssh 1456 vssh 1454 vw $b_{as} CH_3$, (c), (c) 1448 msh 1445 s 1448 vw 1447 m 1445 wsh 1447 wsh 1449 s 1450 s 1451 wsh 1448 vs. 1448 s 1447 wsh b_{o/P} XCH₂ (c), (c) 1430 ssh 1436 wsh 1430 ssh 1439} s 1438 wsh 1438 wsh 1444 wsh b_{I/p} XCH₂ (t), (g) 1440 msh 1442vw 1438 m 1430vssh 1438 wsh 1424 vs 1428 vssh 1428 w 1430} s 1431 vwsh 1430 vwsh 1425} s 1425 m 1426 m 1418 vs 1422 wsh 1420 vssh 1418 1421 vw 1416 vs $w X CH_2(t), (q)$

Observed infrared vibrational frequencies and approximate assignments to the appropriate fundamental modes of vibration of the conformers, cis (c), trans (t) and gauche (g) of ethyl α -haloacetates (cm⁻¹). The notations are: the first parenthesis () is for ethyl α -fluoroacetate and the second () is for ethyl α -chloroacetate, ethyl α -bromoacetate, and ethyl α -iodoacetate. In case there is no parenthesis it means for both conformers.

Table 2 (Contini	ued)
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						1408 vssh	1410 vssh	1412 wsh		vs1428		
1410 vwsh	1415 ssh	1417 vwsh 1405 wsh	1419} s 1409} s	1420 w 1408 wsh	1406 vw	1432 vw	1424 vs.	1430 vs	1410 msh 1409 ssh	1418 vs.	1418 wsh	w XCH ₂ (c), (g)
1398 vw	1400msh	1398 wsh	1399 s	1400 vw	1402 vw	1400ssh	1394 vssh		1392 s	1393 vs.	1393 vw	b _s CH ₃ (t), (g)
	1392 s	1398 wsh	1387 m	1392 vw	1395 vw	1396 ssh	1394 vssh			1389 wsh	1389wsh	b _s CH ₃ (c), (c)
1385 w	1389 s	1388 w	1383 wsh	1382 m	1385 wsh	1386 msh	1381 msh	1384 w	1369vs	1369vs	1374 vw	w CH ₃ (t), (g)
	1379 ssh	1379 msh	1376 m	1375 s	1382 m	1386 msh	1376 msh	1376 w	1369 vs	1369 vs.	1373 w	w CH ₃ (c), (c)
1365 wb	1372 m 1360 msh	1372 m	1365 vwsh		1371 wsh	1369 vw	1370 vs.	1374 w	1362 ssh	1363 wsh	1362 wsh.	w CH ₂ (c), (c)
1326 vw	1336 wsh	1334 wsh	1358 m 1348 msh 1339 w			1356wsh	1357wsh 1344 wsh		1343 vwsh	1345 vw 1337 wsh		w CH ₂ (t), (g)
1300 vw	1300 vsb	1295 vsb	1315 s 1289 vw	1317 vs 1303 vssh 1295 ssh	1317 ssh 1304vssh 1295 ssh	1317 wsh 1308 msh	1316 ssh 1 304vssh	1310 ssh 1311 bssh 1290 s	1308 vssh 1296 vssh	1302 vs 1294 ssh	1309wsh	v C- C (c), (c)
1285 msh 1275 wsh	1272 msh	1275 msh	1279m	1270 vwsh	1270 wsh	1278 s	1272 m	1280 ssh	1277 vsb 1268 vs	1268 vs	1280 vssh 1274 vsb	v C- C (t), (g)
1270 wsh	1270 msh			1267 s	1264 w	1268 vw	1264 vssh	1270 ssh	1273vs	1266 vsb	1271 m	twCH ₂ (t), (g)
1260 m	1260 s	1259 msh		1264 msh	1260 vssh	1258wsh			1256 vssh	1264 vs	1258 msh	twCH ₃ (c,), (c)
1248 w			1251vwsh	1251msh	1252 s	1258 wsh	1252 wsh		1246 msh	1250msh	1246wsh	twCH ₃ (t), (g)
	1239 vssh	1235 wsh	1239 m		1239 msh		1237 s	1221 s	1235 ssh	1238ssh 1226 ws	1236 wsh 1220 w	twCH ₂ (c), (c)
1230 s	1230 vs	1235 wsh										v C- F (t)
1218 wsh	1218 vssh	1218 vs	1212 m 1199 vs 1189 msh	1212 wsh	1216 vwsh 1207 w sh 1195 ssh 1189 vsbsh	1206 ssh	1212 ssh	1212 s		1226 wsh	1220 vwsh 1209 vw	twXCH ₂ (c), (c)
1165 wsh	1175 bwsh	1175 wsh	1169 wsh	1175 ssh 1169 w	1175 vs 1163 msh	1170 ssh.	. 1170 vs	1178msh	1168 vssh	1170vssh	1161 vw	twCH ₃ (t), (g)
1155 w			1153 w 1148 vwsh	1153 msh 1144 wsh	1158 msh 1143 wsh	1160 vssh	1162 vssh	1160 msh	1159 ms	1159 wsh	1156vw	twXCH ₂ (t), (g)
	1128 wsh	1122 vssh	1127 m	1122 vw		1128 ssh	1128 ssh	1130 wsh	1128vssh	1132vssh	1128vwsh	v C- CO ₂ , (c), (c)
1116vwsh	1116 wsh	1116 vssh 1112 vs	1120 vw 1107 vw	1117 vw 1101 vw	1117wsh 1105 vw	1120 s 1112 msh	1118 ssh 1115 vs	1120 vs 1113 vs	1118 vssh 1110 vssh	1118 vssh 1110 vssh	1120 ssh 1119 vwsh	v C- CO ₂ (t), (g)

1087} m	1096 vssh 1086 vs	1097 vssh 1086 vssh	1088vwh	1098 vw	1100 wsh	1087 vw	1083 msh	1087 vwsh	1087 vs	1087 vs	1094 m	r CH ₃ (c), (c)
1071} m	1070 ssh	1070 ssh										ν C- F (c)
1034 vwsh	1041 vssh 1034 vssh	1044 ssh 1038 s	1040 m	1041msh	1048 s 1041 vs	1040 ssh	1038 vs	1040 vs		1040 s	1038 s	ν Ο- CH ₂ (c, (c)
1027vw			1030 vwsh	1029 vs.	1024 wsh	1028 s	1029 vs.	1030 s	1028 vs.	1028vs	1028 msh	v O- CH ₂ (t), (g)
1018vw	1016 vssh	1018 msh		1018 msh	1018 wsh	1010 wsh	1010vssh	1005 wsh	1010 vssh	1010 vssh	1010 msh	r CH ₃ (c),(c)
940 m	947 m	949 w	952 w	955 vw	956 m		928 vs.	930 m	928 w	928 w	930 w	r XCH ₂ (t),(g)
918 vw	923 m	923 m	925 vs.	930 m	930 mb	949 m	948 s	950 vw	952 vs.	950 s	952 vw	r XCH ₂ (c), (c)
870 s	877 ssh	872 vw	879 s	880 wsh	882 w	854 s	860 s		826 m	830 mb		r CH ₂ (t), (g)
860 wsh	860 s	865 m	865 wsh	87 0 m	870 m	892 wsh	895 s		880 s	876 m	882 w	r CH ₂ (c), (c)
818 m	818 wsh	810 s.	810 vw	810 wsh	818 vs.	818 vs.			810 ssh	810 wsh		ν CH ₂ - CH ₃ (t), (g)
	810 w	810 vw		805 wsh	805 msh	812 s	812 wsh		805 msh	807 m	807 vw	v CH ₂ - CH ₃ (c), (c)
	792 w	792 vw		785 s	795 s		790 w	795 w	786 m	785 w	790 vw	b OCO (c), (c)
			778 vs.	775 msh	780 msh							v C- Cl (g)
758 w	760 w	770 w	770 wsh	770 wsh	770 wsh	770 msh	770 wsh		749 s	766 m		b OCO (t,), (g)
720 vw	720 msh	724 vw		700 vw	704} vw		717 msh	722 vw	684 w	684 wsh	684 vw	b C-C-H (t), (c)
			690 s	695 vw	695} vw							v C- Cl (c)
702 vw	699 msh	710 vw	685 ssh	685 wsh		680 vs.	680 msh	685 vw	683 w	683 w	690 [*] m	b C-C-H (t), (g)
	690 m	695 vw	680 wsh	687 wsh	684 vwsh	668 ssh	670 vssh	670 s	654 vs.	. 650 m	655 w	b C- C=O (c), (g)
						662 vw	664 vs.	668 w				v C- Br (g)
620 vw	620 [*] wb	620 [*] wb	620 [*] vw	620 [*] wb	620 [*] w	620 [*] vw	620 [*] vw	620 [*] vw	620 vw	620 [*] vw	620 w	b C- C=O (c), (c)
						556 [*] vw	552 [*] vs.	548 [*] m				v C- Br (c)
590 [*] wb	590 [*] s	606 ^{**} vw	590 [*] vw	590 [*] vw	590 [*] vw	572 ssh	572 ssh	575 w	548 [*] wsh	548 [*] msh		b CC-O (t) , (g)
573 [*] vs.	575 wsh		566 vs 550 vwsh	575 vw 566 vwsh	577 vw 566 vwsh	562 vs.	562 vs.	563 w	565 vw 522 vw	565 msh	568 [*] vw	b CC-O (c) ,(c)
			530 vw 515 vw	530 vw 509 vw	494 vw							bC-C-Cl (c)
									505 [*] s	510 s	522 vw	v C- I (C)
	477 vw	477 vw										b C-C- F (c)
465 vw	465 vw	465 vw	465 vw	465 vw	468 w	461 wsh	461 wsh	465 wsh	460 w	464 w		bCH ₃ -CH ₂ -O (c), (c)

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						455 w	449 w					b C-C-Br (c)
415 vw	415 vw	412 vw	414 vw	414 vw	414 vw	414 vw	413 vw	414 vw	414 vw	412 vw	415 vw	bCH ₃ -CH ₂ -O (t), (g)
									375 vs.	380 sb	390 sb	v C- I (g)
365 w	368 m											bC-C-F(t)
			355 m	353 s	350 wb							b C-C- Cl (g)
						344 s	345 s	349 s				b C-C- Br (g)
									310 sb	330 sb	330 sb	b C-C- I (c)
									290 s	296 sb	285 s	b C-C- I (g)
270 vw 260 vw	270 vw 260 vw	274 vw 262 vw	269 vs.	271 s 262 s	270 wsh 260 vw	285 w 272 w	274 w 270 w	279 w 270 w	270 s 260 s	269 s 256 s	271 vw 260 vw	$\tau \text{ CH}_3\left(t\right),\left(g\right)$
238 m	238 m	240 m	240 w	240 s	238 wb	239 m	239 w	239 w	238 s	238 s	239 w	τ CH ₃ (c), (c)
218 w	218 m	218 m	218 m	219 s	218 m	218 s	218 s	218 s	219 s	219 s	220 s	Skeletal deformation
N.B.: Mode of vib The sub symbols	ration symbols; ; s = symmetric,	; $v =$ stretching, l ass = asymmetri	b = bending, w = ic, i/p = in phase	wagging, tw = t , o/p = out of ph.	wisting, r = rocl ase. The asteris	king Intensity sy k *denotes for l	ymbols; s=stro bands chosen fc	ng, w = weak, v ır thermal work	= very, b = broac :. τ: Torsion.	l, m= medium, :	sh = shoulder.	

(A) **0.2** 0.18 Absorbance 0.16 0.14 \$ 6 7 234 8 0.12 0.1 0.08 0.06 0.19 0 29 0.39 0.49 (ε-1) / (2ε+1) (B) 0.14 234 1 5 6 7 0.12 Absorbance 0.1 0.08 0.06 0.19 0.29 0.39 0.49 (ε-1) / (2ε+1)

Fig. 4. Plots of the absorbance of ν (C=O) bands of the more polar and less polar conformers of ethyl α -haloacetate in various solvents against the solvent dielectric constant function $(\varepsilon - 1)/(2\varepsilon + 1)$: (A) ethyl α -fluoroacetate bands (**a**) at 1803 cm⁻¹ and (**b**) at 1772 cm⁻¹ and (B) ethyl α -chloroacetate bands (**a**) at 1786 cm⁻¹ and (**b**) at 1764 cm⁻¹. The solvent key number is as given in Table 3.

The spectral data for ethyl α -fluoroacetate, ethyl α -chloroacetate and ethyl α -bromoacetate in various solvents are given in Table 3. Ethyl α -iodoacetate was excluded from this table because of the bad data points.

The assignations of the fundamental bands to the appropriate modes of vibration and to the appropriate conformers is based on comparing spectra of these compounds with each other, phase to phase and with spectra of ethylacetate, ethyl α -chloroacetate, ethyl α -trichloroacetate, and with the spectrum of ethyl α trifluoroacetate [18] and ethyl α -cyanoacetate [19], and others in the literature [20-27], in addition to the spectra of propanal [28], 3bromopropene [29], and 1,3-dichloropropane [30]. In the first step, all the halogenated parts were figured out, namely all the XCH₂ modes; the CH₂ stretching, deformation, wagging, twisting, rocking, C-X stretching, bending modes of XCH₂-C=O, and XCH₂-C-O and so on. In the second step, CH₃ and CH₂ of the ethyl group and all relevant modes of vibration were figured out. In the third step, the C-O, CH₂-O stretching and COC bending modes were detected. In fact, all the bands arising from the characteristic groupings CH₃, CH₂ and C=O, XCH₂, C-O, O-CH₂, C-COO, CH₂-CH₃ and C-X were practically figured out through this method.

3.4. Enthalpy difference ΔH°

The enthalpy differences between the conformers have been determined in the vapor, liquid and solid phases using two bands for each molecule identified to arise from two different conformers by using the Van't Hoff equation below

$$\ln \frac{D_{\rm m}}{D_{\rm l}} = \log C - \frac{\Delta H^{\circ}}{RT} \tag{1}$$

where $D_{\rm m}$ and $D_{\rm l}$ are absorptivities (Absorbances) of the more stable and less stable conformers respectively, *C* is a constant comprising molar absorption coefficient ratios of the bands related to the corresponding conformers, partition function ratios and $(\Delta S^{\circ}/R)$. Fig. 5, shows two typical temperature-dependent absorption bands b C–C=O and b C–C–O assigned to cis and trans conformers respectively for ethyl α -fluoroacetate at 620 and 606 cm⁻¹. Linear regression lines were obtained from the plots of $\ln D_{\rm m}/D_{\rm l}$ against T^{-1} . The calculated ΔH° values of these compounds are given in Table 5.

Table 3

Influence of solvents on the intensity of ν (C=O) stretching bands of ethyl α -fluoroacetate at 1803 and 1772 cm⁻¹, ethyl α -chloroacetate at 1786 and 1764 cm⁻¹ and ethyl α -bromoacetate at 1770 and 1752 cm⁻¹ in various solvents. The subscripts t, c and g denote for trans, cis and gauche, respectively.

Solvent	$(\varepsilon - 1)/(2\varepsilon + 1)$	Ethyl α -fluoroacetate		Ethyl α-chlo	roacetate	Ethyl α-broi	moacetate
		Dc	Dt	Dc	Dg	D _c	D_{g}
1. Cyclohexane	0.202	0.166	0.106	0.087	0.100	0.075	-
2. CCl ₄	0.226	0.147	0.096	0.097	0.102	0.069	0.123
3. Benzene	0.23	0.168	0.09	0.106	0.092	0.087	0.125
4. Toluene	0.24	0.166	0.106	0.103	0.083	0.069	0.131
5. Chloroform	0.359	0.141	0.08	0.104	0.093	-	0.119
6. Chlorobenzene	0.377	0.18	0.082	0.102	0.079	0.093	0.127
7. Ethylene dichloride	0.43	0.165	0.075	0.108	0.077	0.095	0.121
8. Acetonitrile	0.48	0.187	0.079	0.123	0.084	0.093	0.120

The enthalpy difference for ethyl α -fluoroacetate was measured in the vapor phase using the b(C–C=O) and b C–C–O bands at 620 and 606 cm⁻¹. The ΔH° value for the cis-trans equilibrium of -3.8 ± 1.7 kJ mol⁻¹ is in good agreement with reported value of -3.6 ± 0.5 kJ mol⁻¹ using ν (C=O) stretching bands [3,31]. The thermal spectral results for all the compounds of this work in the solid, liquid and vapor phases are set out in Table 4.

One can see from Tables 4 and 5, that a reversal in stability is observed in the first compound on passing from the vapor to the liquid and solid phases, where the cis is the more stable in the liquid and solid phases. Ethyl α -chloroacetate and ethyl α bromoacetate show reversal in stability only in the solid phase, indicating preference of stability to the cis in these two compounds respectively. However, the general trend of stability of the predominant conformers the trans for the first compound and gauche for the other three compounds in the vapor phase show a regular increase as the mass of the halogen atom is increased F [trans] < CI [gauche] < Br [gauche] < I [gauche]. In the liquid phase, this trend in the last three compounds is reversed and takes the order Cl > Br > I.

In the solid phase spectrum [non-glassy samples], ethyl α iodoacetate an exception to the first three compounds revealed that the gauche conformer is the more stable conformer as in the liquid and vapor phases. However, the ΔH° values [Table 5] in the solid phase are very low indicating that the conformers of each couple for each compound coexist almost equally with slight bias of the cis conformer in the first three compounds.



Fig. 5. Infrared absorption bands of ethyl α -fluoroacetate 606 and 620 cm⁻¹ recorded at different temperatures in the vapor phase [see Table 2].

3.5. Estimations of the molar energy of activation

The barrier to rotation, which is the molar energy of activation, can be calculated through application of the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

with

$$k = \left(\frac{1}{t}\right) \ln \frac{D_{\infty} - D_0}{D_{\infty} - D_t} \tag{3}$$

where k, A, D_0 , D_t , and D_∞ are rate constant, pre-exponential factor, absorbances at zero time, at time t and at the end of the run respectively. Fig. 6 shows plots of $\ln k$ (k in s⁻¹) against T^{-1} (K^{-1}) for all the compounds of this series. The least squares method was used in the calculations of E_a and the standard errors. The measurements were made in the solid state only at sufficiently low temperature ($-165 \,^{\circ}$ C) for the conformer to manifest itself. Thus, by tracing intensity change of either band with temperature and time it is expected to obtain molar energy of activation value of the relevant conformer. Consequently, the pseudo-thermodynamic parameters of activation ΔS^{\ddagger} , and Gibbs free energy change of activation ΔG^{\ddagger} can be calculated from E_a using the following



Fig. 6. Arrhenius plots of $\ln k$ against T^{-1} , with k in s^{-1} and T in K, for ethyl α -haloacetates in the solid phase. Least squares method was used; the resulting parameters are: (A) for ethyl α -fluoroacetate the slope $m = -0.61 \pm 0.13$ K, intercept $b = -2.94 \pm 0.28$, correlation coefficient r = -0.9791, $\chi^2 = 0.0514$, No. of data points = 10; (B) for ethyl α -chloroacetate; $m = -0.80 \pm 0.03$ K, intercept $b = -2.22 \pm 0.02$, r = -0.98673, $\chi^2 = -0.0284$, No. of data points = 13; (C) for ethyl α -bromoacetate; $m = 0.90 \pm 0.22$ K, $b = -1.30 \pm 0.90$, r = 0.970, $\chi^2 = -9.89 \times 10^{-4}$, No. of data points = 4; (D) for ethyl α -iodoacetate; $m = 1.44 \pm 0.11$ K, $b = 0.50 \pm 0.35$, r = -0.99737, $\chi^2 = -1.09 \times 10^{-4}$, No. of data points = 4.

Table	4
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Temperature dependence of optical densities of couples of some bands arising from different conformers for ethyl α-haloacetates in the solid, liquid, and vapor phase.

Compound	Solid				Liquid	l			Vapor	Vapor			
	T(K)	$D_{\rm t}~590{\rm cm}^{-1}$	$D_{\rm c}~573{\rm cm}^{-1}$	$D_{\rm t}/D_{\rm c}$	T(K)	$D_{\rm t}~590{\rm cm}^{-1}$	$D_{\rm c}~620{\rm cm}^{-1}$	D_t/D_c	T(K)	$D_{\rm t}~606{\rm cm}^{-1}$	$D_{\rm c}~620{\rm cm}^{-1}$	D_t/D_c	
FCH ₂ COOR	108.5 123.0 133.5 142.0 156.5 170.5 182.5 193.5	0.146 0.269 0.234 0.241 0.252 0.251 0.258 0.258	0.162 0.292 0.254 0.256 0.270 0.266 0.272 0.267	0.901 0.921 0.921 0.941 0.933 0.944 0.949 0.966	239 244 254 274 284 294 309 314	0.117 0.115 0.119 0.169 0.197 0.210 0.215 0.302	0.161 0.134 0.131 0.148 0.162 0.157 0.166 0.203	0.727 0.858 0.908 1.142 1.216 1.338 1.295 1.488	313 323 333 353 363 373 388 398	0.42 0.314 0.295 0.271 0.290 0.293 0.398 0.356	0.12 0.101 0.104 0.092 0.107 0.107 0.155 0.152	3.50 3.11 2.84 2.95 2.71 2.74 2.57 2.34	
	<i>T</i> (K)	$D_{\rm g}~590{\rm cm}^{-1}$	$D_{\rm c}~620{\rm cm}^{-1}$	$D_{\rm g}/D_{\rm c}$	<i>T</i> (K)	$D_{ m g}~590{ m cm}^{-1}$	$D_{\rm c}~620{\rm cm}^{-1}$	$D_{\rm g}/D_{\rm c}$	T(K)	$D_{\rm g}~590{\rm cm}^{-1}$	$D_{\rm c}~620{\rm cm}^{-1}$	$D_{\rm g}/D_{\rm c}$	
CICH ₂ COOR	108.5 119.0 128.5 138.5 148.5 158.5 183.5	0.273 0.264 0.246 0.231 0.242 0.256 0.292	0.163 0.152 0.139 0.137 0.135 0.133 0.157	1.675 1.737 1.770 1.686 1.793 1.925 1.860	244 254 259 264 274 284 294 304 314	0.157 0.195 0.220 0.221 0.223 0.224 0.227 0.278	0.068 0.084 0.116 0.128 0.130 0.130 0.134 0.138 0.184	2.309 2.321 1.983 1.957 1.727 1.715 1.672 1.645 1.511	329 349 359 369 379 389 399	0.346 0.346 0.299 0.217 0.198 0.185 0.167	0.270 0.260 0.249 0.191 0.180 0.175 0.163	1.281 1.331 1.201 1.136 1.100 1.057 1.025	
	$T(\mathbf{K})$	$D_{\rm g}~556{\rm cm}^{-1}$	$D_{\rm c}~620{\rm cm}^{-1}$	$D_{\rm g}/D_{\rm c}$	$T(\mathbf{K})$	$D_{\rm g}~552{\rm cm}^{-1}$	$D_{\rm c}~620{\rm cm}^{-1}$	$D_{\rm g}/D_{\rm c}$	$T(\mathbf{K})$	$D_{\rm g}~548~{\rm cm}^{-1}$	$D_{\rm c}~620{\rm cm}^{-1}$	$D_{\rm g}/D_{\rm c}$	
BrCH ₂ COOR	103.5 113.0 123.5 133.5 163.5 173.5 183.5 208.5	0.386 0.390 0.388 0.399 0.405 0.403 0.388 0.397	0.346 0.338 0.328 0.326 0.324 0.306 0.308	1.116 1.154 1.183 1.202 1.242 1.244 1.268 1.289	243.5 251.5 273.5 283.5 293.5 306.5	0.187 0.118 0.109 0.113 0.117 0.113	0.204 0.137 0.147 0.160 0.170 0.168	0.917 0.861 0.741 0.706 0.688 0.673	309 319 339 359 369 389	0.147 0.135 0.092 0.148 0.147 0.140	0.210 0.224 0.198 0.320 0.317 0.354	0.700 0.603 0.465 0.463 0.464 0.395	
	$T(\mathbf{K})$	$D_{\rm g}~548{\rm cm}^{-1}$	$D_{\rm c}~505{\rm cm}^{-1}$	$D_{\rm g}/D_{\rm c}$	$T(\mathbf{K})$	$D_{\rm g}~548~{\rm cm}^{-1}$	$D_{\rm c}~620{\rm cm}^{-1}$	$D_{\rm g}/D_{\rm c}$	$T(\mathbf{K})$	$D_{\rm g}~690{\rm cm}^{-1}$	$D_{\rm c}~568{\rm cm}^{-1}$	$D_{\rm g}/D_{\rm c}$	
ICH ₂ COOR	117.5 128.5 138.5 148.5 158.5 168.5 178.5 188.5	0.198 0.200 0.190 0.186 0.185 0.183 0.183 0.180 0.151	0.265 0.271 0.267 0.266 0.273 0.271 0.277 0.235	0.747 0.738 0.712 0.699 0.678 0.675 0.650 0.643	263.5 273.5 283.5 293.5 303.0 313.0	0.150 0.147 0.137 0.148 0.144 0.142	0.224 0.222 0.216 0.234 0.234 0.234	0.670 0.662 0.634 0.632 0.615 0.607	319 328 339 349 359 369 379 389	0.360 0.404 0.271 0.244 0.228 0.225 0.229 0.215	0.139 0.173 0.121 0.120 0.123 0.127 0.154 0.156	2.590 2.335 2.240 2.033 1.854 1.772 1.487 1.378	

equations [32]:

$$\Delta H^{\ddagger} = E_{\rm a} - RT^0 \tag{4}$$

$$\Delta S^{\ddagger} = R \left[\ln \left\{ \frac{A \ln V_0}{(eRT^0)} \right\} \right]$$
(5)

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T^0 \Delta S^{\ddagger} \tag{6}$$

where h, N_0 , e, and T^0 are Planck's constant, Avogadro's number, e is 2.718 and the temperature 298.15 K, respectively.

The bands used for estimating the molar energy of activation are: 590, 590, 552 (shoulder) and 522 cm⁻¹ for ethyl α -fluoro, ethyl α -chloro, ethyl α -bromo and ethyl α -iodoacetate, respectively. The first band arises from the trans conformer and the others arise from the gauche. The resulting E_a values and the corresponding pseudothermodynamic parameters of activation are given in Table 6. The E_a , ΔH^{\ddagger} and ΔS^{\ddagger} values are increasing as the halogen atomic mass is increased, while ΔG^{\ddagger} values decrease with the third and fourth compounds being exchanging the order of the decreasing trend [see Table 6]. The values of $E_a = 5.1$, 6.7, 7.5 and 12.00 kJ mol⁻¹ for the fluoro, chloro, bromo and iodo compounds respectively are somewhat low indicating that the hindering forces to rotation are not so strong. The calculated potential energy barriers to rotation are: $E_b = 9.2$, 2.1, 4.7 and 6.7 kJ mol⁻¹. They are still lower than the experimental values except for ethyl α -fluoroacetate. The possible sources of hindrances are steric, the partial double bond character where the percentages of which are around 10%, 11%, 14% and 16% for these molecules, respectively, repulsive forces between the halogen and oxygen atoms of the molecule and the interactions between σ^*_{C-X} and $\pi^*_{C=0}$ orbital's and the hyperconjugative effects σ_{C-X} and $\pi^*_{C=0}$.

Table 5

 $Enthalpy \ differences \ of \ the \ cis-trans, \ cis-gauche, \ equilibriums \ of \ ethyl \ \alpha-haloacetates \ in \ the \ solid, \ liquid \ and \ vapor \ phases.$

Compound	ΔH° (kJ mol ⁻¹)		
	Solid phase	Liquid phase	Vapor phase
Ethyl α -fluoroacetate	0.1 ± 0.1	5.0 ± 0.8	-3.3 ± 1.7 ; -3.6 ± 0.5 , Ref. [3,30]
Ethyl α-chloroacetate	0.3 ± 0.2	-3.9 ± 1.3	-4.2 ± 1.7
Ethyl α-bromoacetate	0.3 ± 2.0	-3.2 ± 0.5	-6.7 ± 2.5
Ethyl α-iodoacetate	-0.4 ± 0.1	-1.7 ± 0.0	-9.1 ± 1.7

Table 6

Rate constant k, pre-exponential factor A, energy difference of activation E_a and pseudo-thermodynamic parameters of activation ($\Delta H^{\ddagger}, \Delta S^{\ddagger}, \text{and } \Delta G^{\ddagger}$) of the trans conformer of ethyl α -fluoroacetate and of the gauche conformer of ethyl α -chloroacetate, ethyl α -bromoacetate and ethyl α -iodoacetate in the solid phase.

Compound	$\ln k^*$ (k is in s ⁻¹)	$\ln A (A \text{ is } s^{-1})$	$E_{\rm a}({\rm kJmol^{-1}})$	ΔH^{\ddagger^*} (kJ mol ⁻¹)	ΔS^{\ddagger^*} (J K ⁻¹ mol ⁻¹)	$\Delta {G^{\ddagger}}^*(\mathrm{kJmol^{-1}})$
Ethyl α -fluoroacetate	$(6.78\pm2.92)\times10^{-3}$	-2.94 ± 0.28	5.09 ± 0.37	2.61 ± 0.37	-277.7 ± 2.3	$\textbf{85.4} \pm \textbf{1.1}$
Ethyl α -chloroacetate	$(7.37 \pm 0.04) imes 10^{-3}$	-2.22 ± 0.02	6.67 ± 0.09	4.19 ± 0.09	-271.7 ± 0.2	85.2 ± 0.1
Ethyl α-bromoacetate	0.013 ± 0.019	-1.30 ± 0.90	7.48 ± 1.31	5.00 ± 1.31	-264.0 ± 7.5	83.7 ± 3.6
Ethyl α -iodoacetate	$0.013 \pm 7.82 \times 10^{-3}$	0.50 ± 0.35	12.00 ± 0.62	9.52 ± 0.62	-249.1 ± 2.9	83.8 ± 1.5

The values are calculated at $T^0 = 298.15$ K.



Fig. 7. (A) Plots of the Arrhenius molar enthalpy change of activation ΔH^{\ddagger} and the entropy parameter $T\Delta S^{\ddagger}$ against the polarizability of the halogen atoms at standard temperature $T^0 = 298.15$ K. Linear regression parameters are; the slope $m = 1.42 \pm 0.47$, intercept $b = 0.99 \pm 1.16$, $\chi^2 = 0.552$, r = 0.94961 and No. of data points = 4. For $T\Delta S^{\ddagger}$ parameters, $m = 1.81 \pm 0.41$, $b = -0.85 \pm 1.01$, $\chi^2 = 0.0248$, r = 0.97553, No. of data points = 4. (B) Plot of Arrhenius Gibbs' molar energy of activation ΔG^{\ddagger} against the polarizability of the halogen atoms. ΔG^{\ddagger} parameters, $m = -0.39 \pm 0.23$, $b = 0.86 \pm 0.57$, $\chi^2 = 0.00747$, r = -0.86041, No. of data points = 4.

From Eq. (6), one may expect that the Gibbs isothermal energy change ΔG^{\ddagger} for the kinetic process is the most reliable among the three pseudo-thermodynamic quantities due to the enthalpyentropy cancellation. The ΔH^{\ddagger} and ΔS^{\ddagger} parameters have displayed good linear relationships with the polarizability of the halogen atoms but in the same fashion [Fig. 7A]. On the other hand, the plot of ΔG^{\ddagger} against the polarizability parameter exhibits a linear regression line of negative slope but with appreciable scattering of the data points [see Fig. 6B].

The values of ΔS^{\ddagger} are extremely low because of the preexponential factor values A being very low as given in Table 6. This is a result of the low rate constant values which are in the order of 10⁻⁴ per second and the differences between their consecutive values are very small. However, the low ΔS^{\ddagger} values indicate very small steric effect.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.03.022.

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