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CHARGE DISTRIBUTION IN AND ELECTRIC MOMENTS OF SOME ALIPHATIC ACIDS

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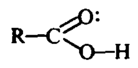
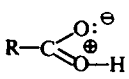
Abstract—Using the treatment of Smith *et al.*, charge distribution in and consequently the dipole moments of several aliphatic acids have been evaluated. The electric moments of chloro (2·86 D), bromo (2·90 D), iodo (2·06 D) and trichloro (3·00 D) acetic acids have been measured in dioxan solution at 35°. The experimental values are compared with those calculated theoretically and discussed in terms of the various possible structures.

INTRODUCTION

ALTHOUGH resonance can occur in carboxylic acids between the structures (a) and (b):



(a)



(b)

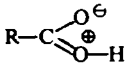
the lack of knowledge of the exact geometry of the —COOH group has prevented the evaluation of the mesomeric moments from dipole moment data. Only recently microwave measurements have been shown to be consistent with a planar structure for formic[2] and acetic[3] acids in which the OH hydrogen is *cis* to the carbonyl oxygen. Further the IR measurements[4] show no absorption peak assignable to *trans* configuration. However, no definite information is available regarding the structure of α-halo substituted acetic acids. In these cases apart from the possibility of the existence of rotational isomers, the O—H group may take up an orientation *trans* to carbonyl since this position can be stabilized by hydrogen bonding with halogen. In order to examine these possibilities and with a view to arrive at their exact structures, the dipole moments of chloro, bromo, iodo and trichloro-acetic acids have been determined in dioxan at 35°. In order to assess the extent of mesomerism in these compounds, the electric moments of a number of aliphatic carboxylic acids have been evaluated by applying the treatment of Smith *et al.*[5]

RESULTS AND DISCUSSION

The results of charge distribution calculations by the Smith *et al.* scheme are summarized in Tables 3 and 4. Table 5 gives the experimental dipole moments and the moments theoretically calculated for various possible configurations of the aliphatic acids.

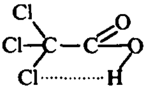
Detailed investigations[11] of the dipole moments of monocarboxylic acids have revealed that these substances are monomeric in very dilute benzene solution or in the vapour at low pressures with an electric moment of about 1·7 D.[12] Since electric moments in dilute dioxan solution are in good agreement[13] with these values it seems likely that the acids remain monomeric in dioxan solution up to perhaps 0·01 mole—fraction of solute and that the interaction with the solvent does not appreciably alter the electric moments from those in the gas phase, as pointed out by Rogers[14] and by Beguin and Gaumann.[15] Recently the electric moments of substituted succinic acids have been measured in dioxan by Thompson *et al.*[16] As mole wt measurements show that the haloacetic acids are monomeric in dioxan, it is reasonable to presume that the effects of solute–solvent interactions on the moment are negligible. This is further borne out by the fact that the dielectric constant varies linearly with the concentration of the solute in the dilutions studied.

From Table 5 it is seen that the difference $\mu_{obs}-\mu_{cal}$ increases as one goes from acetic to crotonic acid and thence to propiolic acid. This difference represents the interaction of C=O and the O—H moments and clearly arises due to the contribution of the mesomeric structure,

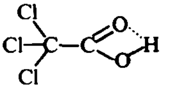


The presence of extended conjugation as in crotonic and propiolic acids enhances the mesomeric moment in order acetic < crotonic < propiolic acid.

The observed moment of trichloroacetic acid (3·0 D) can be accounted for only by assumption of structure (c) in which the hydrogen is *trans* to the carbonyl oxygen in



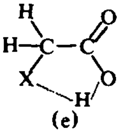
(c)



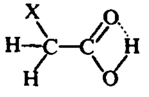
(d)

contrast to structure (d), with its hydrogen *cis* to carbonyl oxygen. The stabilization of structure (c) relative to the *cis* structure (d) probably stems from the enhanced stability of the 5-membered chelate ring produced, consequent upon the formation of the hydrogen bond Cl· · ·H—O. In the *cis* structure too, the carbonyl oxygen can form a hydrogen bond but the resulting chelate ring being 4-membered is less stable. In the case of trifluoroacetic acid, the calculated values for configurations (c) and (d) are almost identical making it difficult to choose between the two. However, the argument adduced for trichloroacetic acid should hold here also and hence trifluoroacetic acid is more likely to exist in configuration (c) than in configuration (d).

In chloro and bromoacetic acids the experimental values agree with those calculated for both positions (e) and (f). By analogy with trichloroacetic acid, structure (e) is more probable for two reasons: (i) the enhanced stability of the 5-membered chelate ring resulting from hydrogen bond formation with halogen, over the 4-membered



(e)



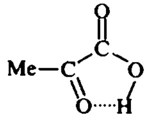
(f)

ring in structure (f), and (ii) since the relatively bulky X is away from carbonyl oxygen the steric interactions are reduced to the minimum.

The possibility of an intramolecular hydrogen bond involving halogen in systems such as those discussed above is indicated by Raman spectra measurements of dioxan solutions of bromo and tribromoacetic acids.[17] A similar situation is encountered in the case of esters of trihaloacetic acids. Unsubstituted aliphatic carboxylic acid esters of the type R_1COOR_2 have electric moments of about 1·7–1·8 D which closely corresponded to the value calculated for a configuration in which the alkyl group (R_2) is *cis* to carbonyl oxygen. But the experimental moments for ethyl trichloroacetate[19] and ethyl perfluorobutyrate[18] could be accounted for only on the assumption of a configuration in which the alkyl group is *trans* to the carbonyl group. The possibility of a C—H···F hydrogen bond being responsible for the highly favoured *trans* configuration has been suggested by Rogers.[18] From IR spectra, Oki and Hirota[20] have inferred the presence of an intramolecular hydrogen bond in a number of α-keto and α-alkoxy carboxylic acids and have pointed out that such intramolecular hydrogen-bonding resulted only when a 5-membered ring could be formed. These ideas clearly support our conclusions.

In the case of iodoacetic acid although the experimental moment is close to the value calculated assuming free rotation along C—C axis, an alternative explanation is preferred in view of the bulky iodine atom hindering free-rotation. The data suggest the absence of stabilization of structure (e) by hydrogen bonding with iodine in line with the known fact that the propensity of H-bonding with iodine is negligible. Calculation of the moment for structure (e) with the O—H bond at 90° to the plane containing $\mathrm{C}\substack{=\mathrm{O}\\ -\mathrm{O}}$ gives a value (2·09 D) close to experiment.

For fluoroacetic acid even more so than for chloro and bromo acids structure (e) should be the dominant one since fluorine enters into hydrogen bonding more readily than chlorine or bromine. A moment of 2·29 D is predicted for fluoroacetic acid. As for pyruvic acid the structure is shown to be



from IR data.[21] A moment of 2·03 D is predicted for pyruvic acid.

TABLE 1. DENSITY AND DIELECTRIC CONSTANT DATA AT 35 ± 0·1°

Chloroacetic acid

Mole fraction $f_2 \times 10^3$	Dielectric constant ε	Density d
10·240	$2{\cdot}2968_3$	$1{\cdot}01997_0$
7·700	$2{\cdot}2710_2$	$1{\cdot}01909_8$
5·788	$2{\cdot}2475_1$	$1{\cdot}01847_9$
3·826	$2{\cdot}2265_5$	$1{\cdot}01776_7$
2·300	$2{\cdot}2103_3$	$1{\cdot}01732_1$

TABLE 1. (*contd.*)

Bromoacetic acid

$f_2 \times 10^3$	ϵ	d
5·503	$2{\cdot}2422_1$	$1{\cdot}02095_8$
4·132	$2{\cdot}2256_2$	$1{\cdot}02007_5$
3·674	$2{\cdot}2177_9$	$1{\cdot}01959_5$
2·300	$2{\cdot}2051_2$	$1{\cdot}01846_0$

Ido acetic acid

$f_2 \times 10^3$	ϵ	d
3·473	$2{\cdot}2183_9$	$1{\cdot}02064_2$
2·432	$2{\cdot}2122_0$	$1{\cdot}01940_8$
1·755	$2{\cdot}2080_6$	$1{\cdot}01858_2$
1·288	$2{\cdot}2048_1$	$1{\cdot}01793_7$
$0{\cdot}583_4$	$2{\cdot}2009_5$	$1{\cdot}01709_4$

Trichloroacetic acid

$f_2 \times 10^3$	ϵ	d
6·054	$2{\cdot}2617_5$	$1{\cdot}02102_8$
4·033	$2{\cdot}2354_0$	$1{\cdot}01950_4$
2·688	$2{\cdot}2223_4$	$1{\cdot}01852_4$
1·590	$2{\cdot}2058_3$	$1{\cdot}01770_7$
0·609	$2{\cdot}1955_2$	$1{\cdot}01679_5$

TABLE 2

Acid	Hedestrand's α	Hedestrand's β	P_T^∞	MR_D	P_0	μ_D
Chloroacetic acid	4·9872	0·3249	180·1	17·84	161·4	2·86
Bromoacetic acid	5·2204	0·8177	187·9	20·66	166·3	2·90
Iodoacetic acid	2·7252	1·1879	111·2	27·17	84·0	2·06
Trichloroacetic acid	5·5084	0·7286	206·4	27·28	177·8	3·00

EXPERIMENTAL

Materials. Dioxan was purified as described[6], $\epsilon_{35^\circ} = 2{,}1890$, $d_{35^\circ} = 1{,}01690$. Iodoacetic acid, a B.D.H. product was recrystallized from pet ether (m.p. 83°). Bromoacetic acid prepared as described,[1] was distilled at reduced press (108–110°/30 mm) prior to use. Chloro- and trichloroacetic acids both E. Merck samples were dried at 25 mm over P_2O_5. The purities of all the acids were checked acidimetrically and all of them were found to be at least 99·9% pure.

Apparatus and methods of measurements. The dielectric constant measurements were made with an a.c. mains operated heterodyne beat apparatus as described.[8] Densities of the solutions were obtained using Ostwald Spengel Pyknometer with ground-in caps at both ends. The polarization of the solute at infinite dilution was obtained using the mean values of Hedestrand constands α and β.[9] Electronic polarization of the solute was calculated by addition of bond refraction values.[10] Atomic polarization was taken as 5% of the electronic polarization. Mol wts of iodo and chloroacetic acids in dioxan were determined by the freezing point method. Tables 1 and 2 summarize the results of the measurements.

TABLE 3. PARAMETERS USED IN CALCULATING THE CHARGE DISTRIBUTION AND DIPOLE MOMENTS BY THE SMITH *et al.* METHOD

Bond a—b	β_{ab}	γ_{ab}†	Bond distance‡ in Å
H—C	0·13	0	1·09
F—C	0·25	−1·44	1·39
Cl—C	0·71	−1·49	1·76
Br—C	0·906	−1·44	1·939
I—C	1·288	−1·73	2·14
O—C	*	*	1·312
H—O	0·169	2·097	0·95
O═C	0·45	−2·32	1·245
C—C	β^C_C 0·718	$\alpha_{CC} = 0$	1·54
C═C	β^C_C 1·70		1·34
C═C	β^C_C 2·84		1·20

* The parameters needed are $\beta^O_C = 0{\cdot}346$ and $\beta^C_O = 0{\cdot}472$ as tabulated by Smith *et al.*[5] and $\alpha_{OC} = 1{\cdot}692$ calculated from the dipole moment of dimethyl ether.[12]

† The parameters β_{HO} and γ_{HO} are derived from H—O bond refraction and dipole moment of water[12] respectively and $\gamma_{O=C}$ from the moment of formaldehyde.[12] All other parameters needed are taken from the Tables given by Smith *et al.*[5]

‡ All the bond distances noted and bond angles required to calculate the moments are taken from literature.[22]

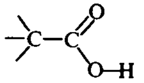
TABLE 4. FORMAL CHARGE DISTRIBUTION IN ALIPHATIC ACIDS

Acid	Oxygen carbo-nyl 1	Oxygen carbo nyl 1′	Oxygen alco-holic	Carbon-1	Carbon-2	Carbon-3	Carbon-2′	Hydro-gen-1	Hydro-gen-2	Hydro-gen-3	Hydro-gen 2′	Hydrogen (hydroxyl)	Halogen
1. Formic acid	−1·600	—	−1·972	1·600	—	—	—	0·208	—	—	—	1·764	—
2. Acetic acid	−1·723	—	−1·990	1·325	0·451	—	—	—	0·063	—	—	1·761	—
3. Propionic acid	−1·733	—	−1·990	1·305	0·378	0·129	—	—	0·049	0·017	—	1·761	—
4. Isobutyric acid	−1·740	—	−1·996	1·290	0·331	0·113	—	—	0·043	0·015	—	1·760	—
5. Trimethylacetic acid	−1·742	—	−2·009	1·287	0·294	0·100	—	—	—	0·013	—	1·757	—
6. Fluoroacetic acid	−1·632	—	−1·947	1·529	1·139	—	—	—	0·148	—	—	1·768	−1·155
7. Chloroacetic acid	−1·656	—	−1·954	1·475	0·949	—	—	—	0·123	—	—	1·767	−0·817
8. Bromoacetic acid	−1·668	—	−1·965	1·448	0·860	—	—	—	0·112	—	—	1·765	−0·666
9. Iodoacetic acid	−1·671	—	1·966	1·443	0·847	—	—	—	0·110	—	—	1·765	−0·639
10. Dichloroacetic acid	−1·616	—	−1·939	1·566	1·256	—	—	—	0·163	—	—	1·769	−0·598
11. Trichloroacetic acid	−1·588	—	−1·926	1·627	1·465	—	—	—	—	—	—	1·771	−0·450
12. Trifluoroacetic acid	−1·467	—	−1·910	1·895	2·303	—	—	—	—	—	—	1·774	−0·864
13. Acrylic acid	−1·726	—	−2·031	1·320	0·369	0·212	—	—	0·048	0·028	—	1·754	—
14. Methocrylic acid	−1·732	—	−1·948	1·308	0·274	0·157	0·093	—	—	0·020	0·012	1·768	—
15. *trans*-Crotomic acid	−1·728	—	−2·032	1·316	0·354	0·182	0·062	—	0·046	0·024	0·008	1·754	—
16. Propiolic acid	−1·725	—	−2·030	1·322	0·376	0·269	—	—	—	0·035	—	1·754	—
17. Pyruvic acid	−1·600	−1·729	−1·972	1·601	1·314	0·448	—	—	—	0·058	—	1·764	—

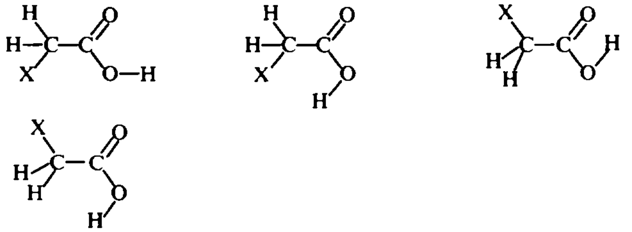
TABLE 5. OBSERVED AND CALCULATED DIPOLE MOMENTS OF ALIPHATIC ACIDS

Acid	μ_{obs}	μ_{cal}	$\mu_{obs}-\mu_{cal}$
Formic acid	1·51	1·28[a]	0·23
Acetic acid	1·73	1·53[a]	0·20
Propionic acid	1·74	1·47[a]	0·27
Isobutyric acid	1·79	1·56[a]	0·23
Trimethylacetic acid	1·70	1·61	0·09
Fluoroacetic acid	—	0·92; 3·29; 2·29; 4·96[b]	
Chloroacetic acid	*2·86	0·39; 2·80; 2·80; 4·90; 1·93[b]	
Bromoacetic acid	*2·90	0·22; 2·99; 2·65; 4·84; 1·80[b]	
Iodoacetic acid	*2·05	0·26, 2·95; 2·72, 4·89; 1·87[b]	
Dichloroacetic acid	—	0·87; 2·59[b]	
Trichloroacetic acid	*3·00	1·76; 3·10[c]	
Trifluoroacetic acid	2·28	2·59; 2·65[c]	
Acrylic acid	—	1·79[a]	
Methyacrylic acid	—	1·63[a]	
Crotonic acid-trans	2·13	1·82[a]	0·31
Propiolic acid	2·08	1·64[a]	0·44
Pyruvic acid	—	2·03[d]	

[a] The values are for the skeleton

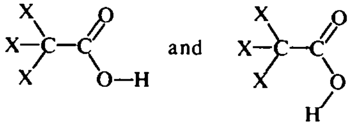


[b] The values are in the order for the skeletons



The last noted value is calculated assuming free rotation using Eyring's formula.[23]

[c] The values are in the order for the skeletons



[d] Calculated for the position shown in page 6.

* Present work. Other values are taken from literature.[12]

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