Aldehydes, Ketones & Acids

Organic compounds containing the carbonyl group >C=O are called ~~carboxyl~~ carbonyl compounds. One of the most important functional groups in organic chemistry.

Classification of Carbonyl Group

(1) Aldehyde : R - CHO

C=O bonded to one H + one C (or H).

(2) Ketone : R - CO - R'

C=O bonded to two carbons.

(3) Carboxylic acid : R - COOH

-COOH = carbonyl + hydroxyl.

Found Everywhere in Nature

- Vanillin (vanilla beans), cinnamaldehyde, benzaldehyde (almonds) - fragrances.
- Formic acid (red ants), acetic acid (vinegar), butyric acid (rancid butter).
- Acetone, formaldehyde - industrial solvents and starting materials for plastics.

Nomenclature - Aldehydes & Ketones

(A) Common names

Aldehyde : replace -ic of acid with -aldehyde.

formic acid --> formaldehyde ($HCHO$)

acetic acid --> acetaldehyde (CH_3CHO)

butyric acid --> butyraldehyde

Ketone : name two alkyl/aryl groups + 'ketone'

$(CH_3)_2C=O$ --> dimethyl ketone = acetone

$Ph-CO-CH_3$ --> methyl phenyl ketone (acetophenone)

Position by Greek letters : α, α', (α = C next to carbonyl C, then beta, gamma, delta ...)

(B) IUPAC names

Aldehyde : alkan~~ol~~ -e + -al

$HCHO$ methanal, CH_3CHO ethanal, CH_3CH_2CHO propanal.

Ketone : alkane -e + -one

CH_3COCH_3 = propan-2-one (acetone).

* CHO numbered = C-1. For ketone : lower locant to C=O carbon.

* Cyclic ketone : C=O C is numbered 1.

* -CHO on ring : ...carbaldehyde suffix.

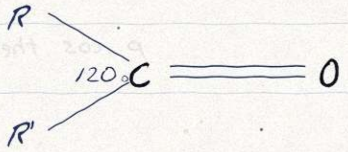
C_6H_5-CHO = benzaldehyde (accepted IUPAC).

Structure of Carbonyl Group

Carbonyl C is sp^2 hybridised.
Forms three sigma bonds + one pi bond
with O (p-p overlap).

Bond angle 120° (trigonal planar)

* C, O, R, R' are coplanar.



Polarity & Resonance

O more electronegative than C -> polar bond.

$C^{(+)} = O^{(-)}$ (dipole)

Resonance : >C=O <--> >C(+) - O(-)

Hence :

- Carbonyl C = electrophilic (Lewis acid)
- Carbonyl O = nucleophilic (Lewis base)
- Substantial dipole moment ; more polar than ethers of comparable mass.

Preparation - Aldehydes (I)

1. Oxidation of 1' alcohol

$$\boxed{R\text{-}CH_2\text{-}OH \longrightarrow R\text{-}CHO \longrightarrow R\text{-}COOH}$$

(PCC stops at the -CHO stage)

PCC ($C_5H_5NH^+$ CrO_3 Cl^-) in CH_2Cl_2
is mild ; stops oxidation at aldehyde.

2. Dehydrogenation of 1' alcohol

Vapours of alcohol passed over Cu / Ag at 573K

$$\boxed{R\text{-}CH_2\text{-}OH \longrightarrow R\text{-}CHO + H_2}$$

<- industrial

3. From acyl chloride - Rosenmund

Hydrogenation of $RCOCl$ over $Pd\text{-}BaSO_4$:

$$\boxed{R\text{-}COCl + H_2 \longrightarrow R\text{-}CHO + HCl}$$

<- Pd / $BaSO_4$
<- (poisoned)

* $BaSO_4$ + S/quinoline poisons Pd to prevent over-reduction to alcohol.

4. From nitrile : Stephen reaction

$$R\text{-}CN \xrightarrow{SnCl_2/HCl} RCH{=}NH \xrightarrow{H_2O} RCHO$$

Also : DIBAL-H reduces -CN or ester -> -CHO.

Preparation - Aldehydes (II)

Aromatic aldehydes from arenes :

5. Etard reaction (Toluene -> PhCHO)

$$\boxed{PhCH_3 \text{ --}CrO_2Cl_2\text{--> complex --H+--> } PhCHO}$$

* Chromyl chloride forms chromium complex,
on hydrolysis gives benzaldehyde.

6. With CrO3 / acetic anhydride

$PhCH_3$ --> $PhCH(OCOCH_3)_2$ --> PhCHO

(benzylidene diacetate)

7. Gatterman - Koch reaction

Direct formylation of benzene with CO + HCl :

$$\boxed{C_6H_6 + CO + HCl \text{ --}AlCl_3/CuCl\text{--> } PhCHO}$$

8. Hydrolysis of benzal chloride

$PhCHCl_2$ --H_2O / OH---> PhCHO

(commercial route via side-chain Cl2.)

9. Hydration of alkynes (gives MeCHO only)

HC -=- CH --H_2O / H_2SO_4 , $HgSO_4$--> CH_3CHO

Preparation - Ketones

1. Oxidation of 2' alcohol

R_2CHOH --CrO_3 / $KMnO_4$--> R_2CO

2. Hydration of alkynes (other)

R-C -=- C-H + H_2O --$HgSO_4$/H+--> R-CO-CH_3

(Markovnikov : OH on more sub'd C).

3. From acyl chloride + R2Cd

2 RCOCl + R'_2Cd --> 2 RCOR' + $CdCl_2$

R'2Cd prepared from 2 R'MgX + CdCl2.

Selective - does not over-react.

4. From nitrile + Grignard

R-CN + R'MgX --> R-C(=NMgX)-R'

--H_3O+--> R-CO-R'

5. Friedel - Crafts acylation

Aromatic ketones (Ar-CO-R) made from arene :

ArH + RCOCl --$AlCl_3$--> Ar-CO-R + HCl

e.g. PhCOCH3 = acetophenone.

Physical Properties (RCHO , R2CO)

State

- $HCHO$ - gas ; CH_3CHO - volatile liquid.
- Higher members - liquid or solid.

Boiling points

$RCHO$, R_2CO > alkanes / ethers (same M)

due to dipole-dipole interaction.

$RCHO$, R_2CO < alcohols (no inter-H-bond)

Order (M 58-60) :

n-butane(273) < $CH_3OC_2H_5$(281)

< propanal(322) < acetone(329)

< n-PrOH(370) (K)

Solubility

Lower members (C1-C4) miscible with water

due to H-bond between H_2O & lone pair on O.

Solubility ~~increases~~ decreases with longer R.

All soluble in benzene, ether, $CHCl_3$.

Odour

Lower aldehydes - pungent sharp smell.

Higher members + cyclic ones - fragrant ;

used in perfumes ; e.g. muscone, jasmine.

Nucleophilic Addition - Mechanism

Carbonyl group is polar -> C is electrophile. Hence undergoes nucleophilic addition (unlike alkenes which undergo electrophilic addition).

Steps

1. Nu- attacks C of >C=0 — — to plane
   (sp^2 --> sp^3 rehybridisation).

2. Tetrahedral alkoxide intermediate :

   $\boxed{R(R')C(Nu) - O(-)}$

3. Alkoxide grabs H+ from medium :

   $\boxed{R(R')C(Nu) - O - H}$ <-neutral <-product

Net : Nu- + H+ added across C=0.

Reactivity Order (RCHO > R2CO)

(a) Steric - 2 bulky R groups hinder Nu attack.

(b) +I effect of 2 R lowers C(+) charge in ketone -> less electrophilic.

Order : HCHO > RCHO > ArCHO R2CO > Ar2CO

(ArCHO less due to +M of ring -> stabilised C+.)

Nucleophilic Addition Reactions

1. Addition of HCN -> Cyanohydrin

$$\boxed{>C{=}O + HCN \xrightarrow{OH^-/CN^-} >C(OH)(CN)}$$

- * Catalysed by base : OH^- generates CN^- , which is a much stronger nucleophile.
- * Cyanohydrins - synthetic intermediates ; hydrolysed to alpha-hydroxy acids.

2. Addition of NaHSO3

$$\boxed{>C{=}O + NaHSO_3 \longrightarrow >C(OH)(SO_3Na)}$$

- * White crystalline addition product.
- * Equilibrium : RCHO >> R_2CO (steric).
- * Used to ~~oxidise~~ purify / isolate aldehydes - reversible with dil HCl / Na_2CO_3.

3. Addition of Grignard reagent

$$\boxed{>C{=}O + R'MgX \longrightarrow R(R')C(OMgX)}$$

$$\boxed{\xrightarrow{H_3O^+} R(R')C(OH) \quad \text{(alcohol)}}$$

HCHO -> 1' OH ; RCHO -> 2' OH ; R_2CO -> 3' OH.

Acetals & Imines

4. Addition of alcohols

Aldehyde + 1 eq $R'OH$ + dry HCl :

$$\boxed{RCHO \dashrightarrow R\text{-}CH(OH)(OR')}$$ <-hemiacetal

Excess $R'OH$ gives :

$$\boxed{R\text{-}CH(OR')_2 \quad \text{(acetal , gem-dialkoxy)}}$$

- * Ketone + ethylene glycol -> cyclic ketal.
- * dry HCl protonates O -> C more electrophilic.
- * Acetals hydrolysed back by aq. mineral acid.

5. Addition of NH_3 derivatives ($H_2N\text{-}Z$)

$$\boxed{>C{=}O + H_2N\text{-}Z \dashrightarrow >C{=}N\text{-}Z + H_2O}$$ <-acid-cat.

Important derivatives :

Z = H (NH_3) --> imine

Z = R ($R\text{-}NH_2$) --> N-sub imine (Schiff base)

Z = OH (NH_2OH) --> oxime

Z = NH_2 (NH_2NH_2) --> hydrazone

Z = NHC_6H_5 --> phenylhydrazone

Z = $NHCONH_2$ --> semicarbazone

Reduction of Carbonyls

2,4 - DNP derivative (Brady's test)

2,4-dinitrophenylhydrazine + >C=0 :

$$\boxed{>C=O + H_2N\text{-}NH\text{-}Ar(NO_2)_2 \dashrightarrow >C=N\text{-}NH\text{-}Ar(NO_2)_2}$$

Orange / yellow / red ppt -> test for carbonyl group (RCHO or R2CO).

6. Reduction to alcohol

$$\boxed{RCHO \xrightarrow{NaBH_4 \text{ or } LiAlH_4} RCH_2OH}$$

$$\boxed{R_2C=O \dashrightarrow R_2CHOH \quad (2'\ OH)}$$

Also : catalytic H2 / Ni-Pt-Pd hydrogenation.

7. Reduction to hydrocarbon (>CH2)

(a) Clemmensen : Zn(Hg) / conc. HCl

$$\boxed{>C=O \dashrightarrow >CH_2 + H_2O}$$ <-acid <-medium

(b) Wolff - Kishner : NH2NH2 / KOH / glycol

>C=0 --> >C=N-NH2 --> >CH2 + N2

* Use Clemmensen for acid-stable ; W-K for base.

Oxidation Tests (RCHO vs R2CO)

RCHO easily oxidised ; R2CO need vigorous conditions and break C-C bond.

8. Tollens' test (silver mirror)

$$\boxed{\mathrm{RCHO} + 2\ [\mathrm{Ag(NH_3)_2}]+ + 3\ \mathrm{OH}-}$$

$$\boxed{\dashrightarrow\ \mathrm{RCOO}- + 2\ \mathrm{Ag(s)} + 4\ \mathrm{NH_3} + 2\ \mathrm{H_2O}}$$

* Aldehyde -> shiny Ag mirror on tube wall.

* Ketones do NOT respond (no -H on C=O).

9. Fehling's test (Cu2O red ppt)

A : aq CuSO4 B : alk. Na-K tartrate (Rochelle)

$$\boxed{\mathrm{RCHO} + 2\ \mathrm{Cu(2+)} + 5\ \mathrm{OH}-}$$

$$\boxed{\dashrightarrow\ \mathrm{RCOO}- + \mathrm{Cu_2O(s)} + 3\ \mathrm{H_2O}}$$

* Reddish brown Cu2O ppt. Aromatic RCHO : give NO response.

10. Haloform reaction (CH3CO- group test)

$$\mathrm{CH_3COR} + 3\ \mathrm{NaOX} \dashrightarrow \mathrm{CHX_3} + \mathrm{RCOONa}$$

Alpha-Hydrogen & Aldol

Acidity of alpha-H

H on C-alpha (adjacent to C=O) is acidic because :

(a) -I & -M effects of carbonyl pull e- away.

(b) Conjugate base = enolate, resonance stabilised over C and O.

>C=O - C(-)H-R <--> >C(-O-) = CH-R

(keto) (enolate)

11. Aldol condensation

Aldehyde / ketone with alpha-H + dilute alkali form beta-hydroxy carbonyl compound (aldol).

$$\boxed{2\ CH_3CHO \ \text{--dil NaOH-->}}$$

$$\boxed{CH_3CH(OH)CH_2CHO \quad \text{(aldol)}}$$

On heating, dehydrates :

$$\boxed{\text{aldol} \ \text{-->}\ CH_3CH{=}CHCHO + H_2O}$$

<-but-2-enal
<-(crotonalde

Cross-aldol : two diff RCHO with alpha-H -> ~~two~~ four possible products (mixture).

Cannizzaro & Other Reactions

12. Cannizzaro reaction

Aldehydes WITHOUT alpha-H undergo self disproportionation in conc. alkali :

$$\boxed{2\ HCHO\ \text{--conc. NaOH-->}}$$

$$\boxed{HCOO^-Na^+ \ + \ CH_3OH}$$

<-salt +
<-alcohol

Mechanism : 1 mol RCHO oxidised -> RCOO-, another reduced -> RCH2OH (hydride shift).

Examples : HCHO, PhCHO, (CH3)3CCHO, (CH3)2C(NO2)CHO - no alpha-H.

13. Electrophilic Substitution (Ar-CO-)

Aromatic RCHO and R2CO undergo E+ on ring.

-CHO and -COR are :

- * deactivating (electron withdrawing -M)
- * meta-directing

$$\boxed{PhCHO + HNO_3/H_2SO_4}$$

$$\boxed{\text{-->}\ m\text{-}NO_2\text{-}C_6H_4\text{-}CHO}$$

Uses + Intro to RCOOH

Uses of HCHO , RCHO , R2CO

- * HCHO (40% aq = formalin) - preserves biological specimens ; makes bakelite, urea-formaldehyde polymers, glues.
- * CH_3CHO - starting material for AcOH, ethyl acetate, vinyl acetate, polymers.
- * PhCHO - perfumery, dyes.
- * Acetone, MEK - industrial solvents.
- * Camphor, vanillin, civetone - flavours / scents.

Carboxylic Acids : R - COOH

- * -COOH = carbonyl + hydroxyl group.
- * Aliphatic R-COOH ; aromatic Ar-COOH.

Common names <- Latin / Greek source :

HCOOH - formic (formica = ant)
CH_3COOH - acetic (acetum = vinegar)
C_3H_7COOH - butyric (butyrum = butter)

IUPAC : alkane -e + -oic acid.

HCOOH = methanoic acid
CH_3COOH = ethanoic acid
HOOC-COOH = ethanedioic acid (oxalic)
PhCOOH = benzenecarboxylic acid (benzoic).

Structure & Physical Properties

Structure of -COOH

Bonds to carboxyl C lie in one plane ;
bond angle 120 deg.

Resonance :

R-C(=O)-OH <--> R-C(-O-)=O(+)H
<--> R-C(+)(-O-)-OH

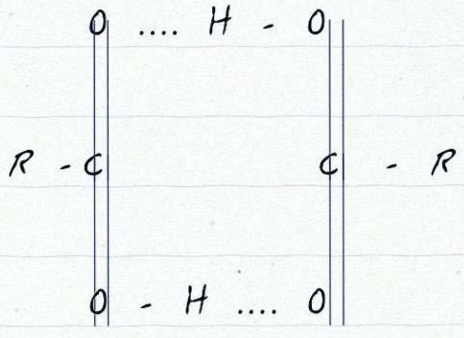
-COOH carbon ~~more~~ less electrophilic than >C=O (lone pair of OH donates into C=O).

Physical Properties

- Lower (C1-C9) - colourless liquids, sharp / unpleasant odour.
- Higher members - waxy solids, odourless.

Boiling Points : RCOOH > ROH > RCHO > RH

Reason : extensive intermolecular H-bonding, exists as DIMERS even in vapour phase.



(dimer)

Preparation of RCOOH

1. From 1' alcohols & aldehydes

RCH_2OH --$KMnO_4$/$K_2Cr_2O_7$--> RCOOH

Mild oxidants like Tollens / Fehling also work
(give $RCOO^-$ in alkaline medium).

2. From alkylbenzenes (side chain ox)

Ph-R --$KMnO_4$ / H^+, heat--> PhCOOH

- * Entire side chain oxidised to -COOH, regardless of length (if 1' or 2' alpha-C).
- * Tertiary alpha-C NOT affected.

3. From nitriles & amides

R-CN --H_2O/H^+--> $R\text{-}CONH_2$ --> RCOOH

4. From Grignard + CO2

RMgX + CO_2 --dry ether--> $RCOO^-MgX^+$

--H_3O^+--> RCOOH (ascending series)

Acidity of Carboxylic Acids

Dissociation

$$\boxed{RCOOH + H_2O <==> RCOO- + H_3O+}$$

$K_a = [RCOO-] [H_3O+] / [RCOOH]$

$pK_a = -\log K_a$ (smaller pK_a = stronger)

* Why so acidic ?

RCOO- stabilised by 2 EQUIVALENT resonance structures - charge spread over 2 electronegative O atoms.

RCOOH > Phenol > ROH

pKa : CH3COOH = 4.76, phenol = 10, ethanol = 16 (effectively neutral).

Phenoxide : -ve charge on C (less stable).

Substituent effects

EWG (Cl, NO_2, CN, F) -> ~~decrease~~ increase acid.

EDG (CH3, OCH3, NH2) -> decrease acidity.

Increasing acidity (alpha-halo):

CH3COOH < ClCH2COOH < Cl2CHCOOH < Cl3CCOOH

Also : Ph < I < Br < Cl < F < CN < NO2 < CF3

Reactions of RCOOH - I

A. Cleavage of O - H bond

1. With active metals (Na, K, Mg, Zn):

$$\boxed{2\,RCOOH + 2\,Na \dashrightarrow 2\,RCOONa + H_2}$$

2. With alkalis (form carboxylate salt):

$$\boxed{RCOOH + NaOH \dashrightarrow RCOONa + H_2O}$$

3. With $NaHCO_3$ / Na_2CO_3 - evolves CO_2 :

$$\boxed{RCOOH + NaHCO_3 \dashrightarrow RCOONa}$$

$$\boxed{+ H_2O + CO_2\ (gas)}$$

<-test for
<--COOH !

(Phenols do NOT release CO_2 with $NaHCO_3$ - distinguishes RCOOH from ArOH.)

B. Acidity comparison summary

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

(decreasing -I as size of X increases)

4-NO_2-PhCOOH > PhCOOH > 4-OMe-PhCOOH

(pKa : 3.41 4.19 4.46)

Reactions of RCOOH - II

C. Cleavage of C - OH bond

1. Formation of anhydride :

$2\ RCOOH$ --P_2O_5 or H_2SO_4/heat-->

$(RCO)_2O + H_2O$

2. Esterification (with R'OH / H+):

$RCOOH + R'OH$ <==> $RCOOR' + H_2O$

H2SO4 <- conc.

Mechanism : nucleophilic acyl substitution - protonation of >C=O -> Nu attack by R'OH -> tetrahedral intermediate -> -OH leaves as H2O.

3. With PCl5 , PCl3 , SOCl2 :

$RCOOH + PCl_5$ --> $RCOCl + POCl_3 + HCl$

$RCOOH + SOCl_2$ --> $RCOCl + SO_2 + HCl$

* SOCl2 preferred - by-products are gases.

4. With NH3 -> amide (via salt then heat).

Reactions of RCOOH - III

D. Reactions involving -COOH itself

1. Reduction (to 1' alcohol):

$\boxed{RCOOH \xrightarrow{LiAlH_4 \text{ or } B_2H_6} RCH_2OH}$

* B2H6 better - does NOT reduce ester / -NO2 ;
NaBH4 cannot reduce -COOH.

2. Decarboxylation (-CO2):

$\boxed{RCOONa \xrightarrow{NaOH / CaO,\ heat} R\text{-}H + Na_2CO_3}$

NaOH + CaO (3:1) = sodalime.

Kolbe electrolysis (aq RCOONa):

$\boxed{2\ RCOO^- \xrightarrow{electrolysis} R\text{-}R + 2\ CO_2 + 2\ e^-}$

E. Substitution in hydrocarbon part

3. Hell - Volhard - Zelinsky reaction :

$\boxed{RCH_2COOH + X_2 \xrightarrow{red\ P} RCHX\text{-}COOH + HX}$

(X = Cl, Br ; alpha-halogenation, -I increases acid.)

Uses + Distinguishing Tests

Uses of $RCOOH$

- $HCOOH$ (methanoic) - leather, dyeing, electroplating, rubber industry.
- CH_3COOH (ethanoic) - solvent, vinegar.
- $(CH_2)_4(COOH)_2$ (adipic) - Nylon 6,6.
- Esters of $PhCOOH$ - perfumery ; $PhCOONa$ - food preservative.
- Higher fatty acids - soaps & detergents.

Key Distinguishing Tests

1. $RCHO$ vs R_2CO :

   Tollens (Ag mirror), Fehling (Cu_2O ppt) :
   $RCHO$ +ve ; R_2CO -ve.

2. $-CHO$ / $-COR$ vs others :

   2,4-DNP → orange / red ppt (only carbonyl).

3. CH_3CO- group (or CH_3CHOH-) :

   Iodoform test → yellow CHI_3 ppt.

4. $RCOOH$ vs $ArOH$:

   $NaHCO_3$ fizz (CO_2) → $RCOOH$ only.

5. $PhCOOH$ vs $PhOH$: $FeCl_3$ violet → phenol.

Worked Example 1

Q. Give IUPAC names :

(i) $CH_3CH(CH_3)CH_2CH_2CHO$

(ii) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$

(iii) $CH_3CH{=}CHCHO$ (iv) $CH_3COCH_2COCH_3$

Answer

(i) Number from -CHO carbon (=C1):

C1(CHO)-C2-C3-C4(CH_3)-CH_3 = 5 carbons

Methyl at C-4 -> 4-Methylpentanal.

(ii) Longest C-chain through C=O ; lower locant to C=O. Chain has 6 C, C=O at C-3, ethyl at C-$\overset{*}{4}$, Cl at C-6 :

6-Chloro-4-ethylhexan-3-one.

(iii) $CH_2{=}CHCHCHO$ with C=C and -CHO ;

chain 4C : ~~but-3-enal~~ but-2-enal.

(-CHO is C1, double bond between C2-C3.)

(iv) 5C, C=O at C-2 and C-4 :

pentane-2,4-dione.

Always number from end nearest principal functional group (-CHO > -CO- > -OH).

Worked Example 2

Q. Compound (A), MF $C8H8O$:

- gives orange-red ppt with 2,4-DNP
- yellow ppt with $I2$ / NaOH (iodoform +)
- does NOT reduce Tollens or Fehling
- does NOT decolourise $Br2$-water
- drastic oxidation -> acid (B) $C7H6O2$

Identify (A) and (B).

Solution

+ 2,4-DNP -> C=O present (RCHO or R2CO).

- Tollens / - Fehling -> must be a ketone.

+ iodoform -> $CH3CO$- group present.

- $Br2$ water -> no alkene / alkyne ; high DoU comes from an aromatic ring.

(B) $C7H6O2$ = benzoic acid PhCOOH.

Thus (A) = $PhCOCH3$ (acetophenone).

$$\boxed{PhCOCH_3 + 3\ I_2/NaOH \longrightarrow PhCOONa + CHI_3 \text{ (yellow)}}$$

$$\boxed{PhCOCH_3 \xrightarrow{CrO_3,\ heat} PhCOOH \qquad (B)}$$

Degree of unsaturation = $(2*8+2-8)/2 = 5$

-> 4 for benzene ring + 1 for C=O. OK

Confirmed : acetophenone -> benzoic acid.

Worked Example 3

Q. Arrange in increasing order of acid strength :

CH3CH2CH(Br)COOH (A)
CH3CH(Br)CH2COOH (B)
(CH3)2CHCOOH (C)
CH3CH2CH2COOH (D)

Approach

Acid strength depends on stability of RCOO-.

Two factors :

(i) EWG (Br) -> stabilises carboxylate (-I)
(ii) Closer EWG to -COOH -> stronger -I effect.
(iii) EDG (extra -CH3) -> destabilises ; weaker.

Analysis

A : Br on alpha-C -> strong -I , close ;
B : Br on beta-C -> -I weaker (farther);
C : isopropyl (extra -CH3 branching) - no Br
but more +I -> destabilises RCOO- most;
D : n-propyl, no Br -> similar but +I less.

$$\boxed{\text{Order : C < D < B < A}}$$ <-increasing <-acidity

i.e. (CH3)2CHCOOH < n-PrCOOH < beta-Br < alpha-Br butanoic acid.