TABLE III

Effect of adjacent carbon groups on the rate of organic transformations [a]

Decarboxylation of a carboxylic acid, R–COOH or R–COO^-		Dehydration of an alcohol, R–$CR^{\prime}R^{\prime\prime}$–OH		Deacylation, isomerization and aldolization of a ketone or aldehyde, R_2>C=O or R–CHO	
Substance	Estimated $t_{1/2}$–50 °C	Substance	Estimated $t_{1/2}$–50 °C	Substance	Estimated $t_{1/2}$–50 °C
acetic acid	3×10^{27} s	1°-alcohol (ethanol, propanol,	[1×10^{18} s][g]	2-decanone (deacyl., isomer.)	no react. (250 °C)
acetate	2×10^{25} s	decanol, phenylethanol)		decanal (0.01 M aldoliz.)	2×10^{6} s (250 °C)
		3°-alcohol (t-butanol)	1×10^{8} s	2-decanone (0.01 M aldoliz.)	4×10^{7} s (250 °C)
acetoacetic acid	4×10^{3} s	3-hydroxy-propanal	5×10^{5} s	acetylacetone (deacylation)	8×10^{5} s
acetoacetate	2×10^{5} s				
lactic acid	2×10^{13} s [b]	ethylene glycol	insuff. data	glyceraldehyde (isomerization)	5×10^{6} s
lactate	[2×10^{13} s][c]			glycolaldehyde (0.01 M aldoliz.)	2×10^{7} s
tartronate semialdehyde	[10^{3} s][d]	glyceraldehyde	9×10^{5} s	α-hydroxymalonaldehyde	no data found
pyruvic acid	1×10^{4} s [e]	glycolaldehyde	aldolizes	glyoxal (intramolec. redox)	3×10^{6} s
pyruvate	6×10^{5} s [e]			pyruvaldehyde (intramolec. redox)	2×10^{6} s
oxalic acid	6×10^{9} s	lactic acid	2×10^{13} s [b]	glyoxylate	decarboxylates
$oxalate^{-2}$	[6×10^{11} s][f]	lactate	[2×10^{13} s][c]		
malonic acid	4×10^{6} s	β-hydroxy acids (β-hydroxybutyric		malonic semialdehyde	no data found
$malonate^{-1}$	6×10^{6} s	acid, $malate^{-1}$, 2-deoxygluconic acid)	[6×10^{12} s][h]		

[a] Unbracketed half-lifes were estimated by extrapolation using Arrhenius plots. Bracketed half-lifes were estimated by extrapolation using the Arrhenius plot slope of a related reaction (reactions noted below).

[b] Half-life was estimated using the most recent study indicating an 1/1 ratio of decarboxylation to dehydration (Lira and McCrackin, 1993).

[c] Half-life of lactate was estimated using the slope of the Arrhenius plot of lactic acid (Lira and McCrackin, 1993).

[d] Half-life of tartronate $semialdehyde^{-1}$ was estimated using the slope of the Arrhenius plot of related β-ketoacids.

[e] Pyruvic acid decarboxylation yielded acetate instead of the expected acetaldehyde (see discussion in text).

[f] Half-life of $oxalate^{-2}$ was estimated using the slope of the Arrhenius plot of oxalic acid.

[g] Half-life of 1°-alcohols was estimated from the joint Arrhenius plot of the alcohols listed.

[h] Half-life of β-hydroxy acids was estimated from the joint Arrhenius plot of the acids listed.