

TABLE I  
Rates of decomposition of organic compounds

Group type (R = H or hydrocarbon) Example reactants	Type of reaction <sup>a</sup>	Conditions ( $t_{1/2}$ at given temp.) <sup>b, c</sup>	$t_{1/2}$ at 50 °C <sup>d</sup>	References
HOOC-COOH				
1. oxalic acid	decarbox.	0.5 M aq. 132, 144, 152, 164, 174 °C (12.6, 3.25, 1.45, 0.43, 0.17 h)	200 y	(Lutgert and Schroer, 1940)
2. oxalate <sup>-2</sup>	decarbox.	0.5 M aq 160 °C [2.28 d]		(Dinglinger and Schroer, 1937)
R-CO-COOH				
3. pyruvic acid	decarbox.	0.25 M aq. 210, 220, 230, 240 °C (257, 224, 187, 161 s)	0.2 d	(Belsky <i>et al.</i> , 1999)
4. pyruvate	decarbox.	0.25 M aq. 220, 230, 240 °C (1000, 856, 630 s)	6.3 d	(Belsky <i>et al.</i> , 1999)
5. glyoxylate	decarbox.	5 mM aq. 25 °C-buf. pH 8 [ $>123$ d]		(Halliwell and Butt, 1972)
6. benzoylformic acid	decarbox., decarbon.	0.9 M aq. 200 °C [5.72 d]		(Katritzky <i>et al.</i> , 1990b)
>COH-COOH				
7. lactic acid	decarbox., dehydr., decarbon.	0.4 M aq. 320, 340, 360, 380, 400 °C [1940, 1020, 358, 134, 78 s]	10 <sup>6</sup> y	(Lira and McCrackin, 1993)
8. lactic acid	decarbox., dehydr., decarbon.	0.1 M aq. 350, 365, 375, 385, 400 °C [168, 91, 66, 38, 24 s]	10 <sup>5</sup> y	(Mok <i>et al.</i> , 1989)
9. lactate	decarbox., dehydr., decarbon.	0.1 M aq. 385 °C [263 s]		(Mok <i>et al.</i> , 1989)
10. 3-deoxy-mannonic acid	decarbox., other react.	0.05 M aq. 340 °C (100 s)		(Luijckx <i>et al.</i> , 1995)
11. mandelic acid	decarbox., decarbon.	0.9 M aq. 200, 250 °C [8.6, 1.7 d]	10 <sup>5</sup> y	(Katritzky <i>et al.</i> , 1990b)
≥C-CR <sub>2</sub> -COOH				
12. acetic acid	decarbox.	1.0 M aq. 400, 422, 440 °C (170, 40, 16 d)	10 <sup>20</sup> y	(Palmer and Drummond, 1986)
13. acetate	decarbox.	1.0 M aq. 340, 359, 389 °C (51, 16, 2.6 d)	10 <sup>18</sup> y	(Palmer and Drummond, 1986)
14. 1-decanoic acid	no reaction	0.8 M aq. 250 °C [13.5 d-lower limit]		(Siskin <i>et al.</i> , 1990a)
15. benzoic acid	decarbox.	1.2 M aq. 350 °C-6 h [174 d]		(Katritzky <i>et al.</i> , 1990c)
16. phenylacetic acid	decarbox.	1.0 M aq. 250 °C-5 d [4.74 y]		(Katritzky <i>et al.</i> , 1990a)
17. γ-hydroxybutyric acid	no reaction	0.1 M aq. 385 °C [30 s-lower limit]		(Mok <i>et al.</i> , 1989)
HOOC-CR <sub>2</sub> -COOH				
18. malonic acid	decarbox.	aq. 120, 160, 190, 210 °C (1350, 31, 2.9, 1.0 s)	46 d	(Maiella and Brill, 1996)
19. malonate <sup>-1</sup>	decarbox.	aq. 120, 160, 190, 210 °C (1380, 43, 5.4, 1.4 s)	71 d	(Maiella and Brill, 1996)
20. malonate <sup>-2</sup>	no reaction	0.5 M aq. 125 °C [48 h-lower limit]		(Fairclough, 1938)
>COH-CR <sub>2</sub> -COOH				
21. 2-deoxy-gluconic acid	decarbox., other react.	0.05 M aq. 340 °C (20 s)		(Luijckx <i>et al.</i> , 1995)
22. β-hydroxybutyric acid	dehydr.-decarbox.	0.1 M aq. 385 °C-32 s [13 s]		(Mok <i>et al.</i> , 1989)
23. malate <sup>-1</sup>	dehydr.	2 mM aq. 175 °C-buf. pH 5 (8.0 d)		(Bender and Connors, 1962)
-CO-CO-				
24. glyoxal	intramol. redox	0.02-20 mM aq. 50 °C-pH 9, 10, 11 (5.8, 0.40, 0.036 h)	(37 d-pH 7)	(Fratzke, 1986)
25. pyruvaldehyde	intramol. redox	1 mM aq. 180, 200, 220, 240 °C (462, 231, 109, 41 s)	(21 d)	(Bonn <i>et al.</i> , 1985)
26. pyruvaldehyde	intramol. redox	0.03 M aq. 20 °C [3.5 d]		(Weber, 1982)
27. phenylglyoxal	intramol. redox	0.06 mM aq. 35 °C-pH 7 [3.0 y]		(Hine and Koser, 1971)
>COH-CO-				
28. glycolaldehyde (see Table II for sugars)	aldol.	0.03 M aq. 50 °C-pH 6 [285 d-0.01 M bimol]	285 d	(Weber, 2001a)
≥C-CO-				
29. 2-decanone	aldol.-dehydr. no hydro. deacylation	0.9 M aq. 250 °C [175 y-0.01 M bimol] 0.9 M aq. 250 °C [1.0 yr unimol-lower limit]		(Siskin <i>et al.</i> , 1990a)
30. cyclohexyl-phenyl- ketone	no reaction	0.8 M aq. 250 °C [5.5 d-lower limit]		(Siskin <i>et al.</i> , 1990b)
31. acetophenone	aldol.-dehydr.	1.2 M aq. 250 °C [101 y-0.01 M bimol]		(Katritzky <i>et al.</i> , 1990d)

TABLE I  
(Continued)

Group type (R = H or hydrocarbon) Example reactants	Type of reaction <sup>a</sup>	Conditions ( $t_{1/2}$ at given temp.) <sup>b, c</sup>	$t_{1/2}$ at 50 °C <sup>d</sup>	References
32. acetaldehyde	aldol.-dehydr., decarbon. (2.5/1)	0.5 M aq. 385 °C [1.9 h–0.01 M bimol] and [262 s–unimol]		(Ramayya <i>et al.</i> , 1987)
33. 1-decanal	aldol.-dehydr., intermol. redox, decarbon. (45/1)	0.9 M aq. 250 °C [15 d–0.01 M bimol]		(Siskin <i>et al.</i> , 1990a)
34. phenylacetaldehyde	aldol.-dehydr.	1.2 M aq. 100 °C [248 d–0.01 M bimol]		(Katritzky <i>et al.</i> , 1990a)
35. benzaldehyde	intermol. redox	1.3 M aq. 250 °C [151 d–0.01 M bimol]		(Katritzky <i>et al.</i> , 1990c)
>COH-COH<				
36. ethylene glycol	radical fragm.	0.5 M aq. 385 °C [419 s]		(Ramayya <i>et al.</i> , 1987)
37. glycerol	dehydr., radical fragm.	aq. 500 °C [162 s]		(Antal <i>et al.</i> , 1985)
38. phenylethane-1,2-diol	dehydr.-aldol.	1.0 M aq. 200 °C [1.8 h]		(Katritzky <i>et al.</i> , 1990b)
≥C-COH<				
39. ethanol	dehydr., dehydrog., radical fragm.	1.0 M aq. 500 °C [2260 s]		(Ramayya <i>et al.</i> , 1987)
40. n-propanol	dehydr., radical fragm.	1.0 M aq. 500 °C [345 s]		(Ramayya <i>et al.</i> , 1987)
41. 1-decanol	intermol. redox-decarbon., dehydr. (7/1)	0.9 M aq. 250 °C [498 y–0.01 M bimol] and [3.1 y–unimol]		(Siskin <i>et al.</i> , 1990a)
42. t-butanol	dehydr.	0.05 M aq. 225, 250, 320 °C [142, 57, 3 s]	4.1 y	(Xu <i>et al.</i> , 1994, 1997)
43. cyclohexanol	dehydr.	0.05 M aq. 300 °C [6230 s]		(Kuhlmann <i>et al.</i> , 1994)
44. 2,2-dimethyl-propanol	no reaction	0.5 M aq. 300 °C [1 h–lower limit]		(Kuhlmann <i>et al.</i> , 1994)
45. pentaerythritol	no reaction	0.5 M aq. 300 °C [1 h–lower limit]		(Kuhlmann <i>et al.</i> , 1994)
46. 1,4-butanediol	no reaction	0.1 M aq. 250 °C [100 s–lower limit]		(Antal <i>et al.</i> , 1990)
47. benzyl alcohol	intermol. redox	1.2 M aq. 250 °C [13 d–0.01 M bimol]		(Katritzky <i>et al.</i> , 1990c)
48. 2-phenylethanol	dehydr.	1.3 M aq. 250 °C [313 d]		(Katritzky <i>et al.</i> , 1990a)
≥C-C≤				
49. cyclohexylbenzene	no reaction	0.9 M aq. 250 °C [5.5 d–lower limit]		(Siskin <i>et al.</i> , 1990b)
50. (cyclohexylmethyl)- benzene	no reaction	0.8 M aq. 250 °C [5.5 d–lower limit]		(Siskin <i>et al.</i> , 1990b)
51. benzene	no reaction	1.8 M aq. 250 °C [5 d–lower limit]		(Katritzky <i>et al.</i> , 1990c)
52. toluene	no reaction	1.6 M aq. 350 °C [14 d–lower limit]		(Katritzky <i>et al.</i> , 1990c)
53. ethylbenzene	radical fragm.	1.3 M aq. 250 °C [1316 d]		(Katritzky <i>et al.</i> , 1990d)
54. 1-decene	dimeriz., isomeriz. (1/1)	1.0 M aq. 250 °C [36 y–0.01 M bimol] and [93 d unimol]		(Siskin <i>et al.</i> , 1990a)
One carbon compd.				
55. formic acid	decarbox., dehydr.	1.0 M aq. 290, 300, 310, 320 °C (385, 248, 198, 177 s)	310 d	(Maiella and Brill, 1998)
56. formic acid	decarbox., dehydr.	2–15 mM aq. 320, 340, 360, 380, 420 °C (14, 7.1, 5.5, 4.2, 1.0 s)	325 d	(Yu and Savage, 1998)
57. formate	no reaction	1.0 M aq. 320 °C [35 sec–lower limit]		(Maiella and Brill, 1998)
58. formaldehyde	intermol. redox	4.5 M aq. 250 °C (1.2 h)		(Tsuji <i>et al.</i> , 1999)
59. formaldehyde	CO + CO <sub>2</sub> + H <sub>2</sub>	0.25 M aq. 385 °C (8.8 s)		(Ramayya <i>et al.</i> , 1987)
60. formaldehyde	no reaction	0.1 M aq. 100 °C [16 h–lower limit]		(Schwartz and de Graaf, 1993)
61. methanol	no reaction	1.0 M aq. 500 °C [60 s–lower limit]		(Ramayya <i>et al.</i> , 1987)
62. methane	dehydrog.	gas at 800, 900, 1000 °C (108, 34, 4 h)	10 <sup>19</sup> y	(Sackett, 1995)

<sup>a</sup> Abbreviations: decarboxylation (decarbox.), decarbonylation (decarbon.), dehydration (dehydr.), intramolecular reduction-oxidation (intramol. redox), aldolization (aldol.), intermolecular reduction-oxidation (intermol. redox), radical fragmentation (radical fragm.), dehydrogenation (dehydrog.), dimerization (dimeriz.), hydrolytic deacylation (hydro. deacylation). Reactions joined by a dash are sequential. The pathway relationships of reactions separated by a comma are unspecified. In a few cases the ratio of bimolecular to unimolecular reactions is given at the end of the reaction list.

<sup>b</sup> Half-lives enclosed in parentheses were calculated from measured reaction rate constants (see Methods for all calculations).

<sup>c</sup> Half-lives enclosed in brackets were estimated from product yields. Half-life lower limits ( $t_{1/2}$ -lower limit) were calculated for non-reactions where no product was detected. Bimolecular (biomol) half-lives were calculated assuming a 0.01 M initial reactant concentration.

<sup>d</sup> Half-lives at 50 °C were estimated by extrapolation using Arrhenius plots.