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c-$C_5H_5^+$ + e → c-C_5H_4 +H (1)
→ c-C_5H_3 +H_2 (2)
→ C_3H_3 + C_2H_2 (3)
→ C_4H_2 + CH_3 (4)
→ C_3H_4 + C_2H (5)
→ C_4H_4 + CH (6)
→ c-C_5H_3 + 2H (7)
→ c-C_3H_2 + C_2H_2 + H (8)
→ C_5H_2 + H_2 +H (9)

Enthalpies of reactions:

ΔH^o_r (1) = - 81 kcal/mol (- 3.5 eV)(a)
ΔH^o_r (2) = -91 [-71] kcal/mol (-3.9 [-3.1] eV)(b)
ΔH^o_r (3) = - 123 [-108] kcal/mol (- 5.3 [- 4.7] eV)(c)
ΔH^o_r (4) = - 113 [-93] kcal/mol (-4.9 [-4.0] eV)(d)
ΔH^o_r (5) = - 79 [-59] kcal/mol (-3.4 [-2.6] eV)(e)
ΔH^o_r (6) = - 48 [-28] kcal/mol (- 2.1 [-1.2] eV)(f)
ΔH^o_r (7) = +13 kcal/mol (+ 0.6 eV)(g)
ΔH^o_r (8) = - 28 [-8] kcal/mol (- 1.2 [-0.3] eV)(h)
ΔH^o_r (9) = - 33 [-13] kcal/mol (- 1.4 [-0.6] eV)(i)

Reactions involving cyclic cyclopentadienyl radical (c-C_5H_5) have been considered. This isomer is the most stable C_5H_5 isomer (formation enthalpy of 65 kcal/mol whereas the second more stable linear isomer requires 95kcal/mol [1]). This isomer is likely to be populated because the cyclic five-membered $C_5H_5^+$ is the second most stable isomer of the cation, close (3kcal/mol) from the vinylcyclopropenyl cation [2].

The quoted enthalpies have been calculated using the ionisation energy of c-C_5H_5 (8.4 ±0.05 eV [1]) and formation enthalpies of parent and products from the literature (see values given in comments). Negative values correspond to exoergic reactions. Estimated error bars on ΔHr values: ~ 10kcal mol^{-1} (0.4 eV). This error does not take into account the uncertainty about barriers (taken equal to 20 kcal/mol when no data available).

On the basis of reaction enthalpies values, we deduce that channels (7)-(9) involving three fragments (and other less favourable three-fragments channels not reported) will not contribute significantly to the exit channels. Concerning two-fragments channels, a strong correlation between branching ratios and exothermicities has been demonstrated and explained with the use of a statistical model recently [8]. Accordingly we propose the following branching ratios.

Recommended Branching ratios:

(3) = 0.50
(1)=0.25
(4)=0.25

Reliability of Branching Fractions: ±0.15 (uniform)

Comments

(a) Formation enthalpy of c-C_5H_4 is 126 kcal/mol [1]; standard enthalpy of H is 52 kcal/mol [3-4].

(b) Formation enthalpy of c-C_5H_3 is 168 kcal/mol [1]. Value between bracket includes a barrier (H_2 formation), estimated to 20 kcal/mol.

(c) Decomposition of c-C_5H_5 into acetylene (C_2H_2) and propargyl (C_3H_3) has been shown to be a multistep process involving hydrogen-atom shift and ring opening [5]. The first value of reaction enthalpy does not include barriers (and use formation energies of 54 kcal/mol and 82 kcal/mole for C_2H_2 and C_3H_3 respectively [3-4]) whereas the second value between brackets includes the calculated barriers of [5].

(d) Formation enthalpies of C_4H_2 (1,3-butadiyne) and CH_3 (methyl) equal to 111 kcal/mol and 35 kcal/mol respectively [4]. Value between bracket includes a barrier, estimated to 20 kcal/mol.

(e) Formation enthalpies of 136 kcal/mol and 44 kcal/mol have been used for C_2H and C_3H_4 (allene, the lowest energy isomer) respectively [3]. Value between bracket includes a barrier, estimated to 20 kcal/mol.

(f) Formation enthalpies of 142 kcal/mol and 69 kcal/mol have been used for CH and C_4H_4 (vinylacetylene, the most stable isomer [7]) respectively [3]. Value between bracket includes a barrier, estimated to 20 kcal/mol.

(g) Formation enthalpy of c-C_5H_3 is 168 kcal/mol [1].

(h) Formation enthalpy of c-C_3H_2 is taken equal to 125 kcal/mol [3,6]. Value between bracket includes a barrier, estimated to 20 kcal/mol.

(i) Formation enthalpy of C_5H_2 is taken equal to 174 kcal/mol (three membered cyclo [1]). Value between bracket includes a barrier, estimated to 20 kcal/mol.

References

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