Redoxpotential and resonance energy of certain quinones.

by

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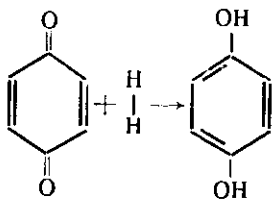
The reaction which takes place when a quinone is hydrated to the corresponding hydroquinone is symbolised by the following equation:



The energy change accompanying this reaction can be calculated from bond energy data. According to the above equation one H—H, two C=O, two C=C and four C—C bonds must be broken and two O—H, two C—O, three C=C and three C—C bonds must be rebuilt. Since in all reactions in which a paraquinone is hydrated to hydroquinone the same structural change occurs, the energy change calculated from bond energies will have the same value. Correspondingly the redoxpotential calculated from this value would have the same value in all cases. (The entropy in these reactions has a standard value[1].) Various quinone-hydroquinone systems however have different redoxpontential values. The resonance energies are responsible for this fact. These energy values must be included into calculations useing bond energy data.

In the following table some data are given to show how the resonance energy values are related to the redoxpotential values of some quinone-hydroquinone redox-systems. In col. 1. the redoxpotential values[2], in col. 2. the resonance energy

values of quinones and hydroquinones, and in col. 3 the difference of these resonance energy values are given. On comparing col. 1. and 3 it can be seen that the redoxpotential becomes smaller and smaller as the difference of the resonance energies between quinones and hydroquinones diminishes. Thus the redoxpotential seems to be a function of the resonance energy.

Table.

	Redoxpot. in Volts	Resonance energy in kcal./mole	Difference of resonance energies.
Quinone	0,681	— 3.3	51,0
Hydro „		47,7	
Toluquinone	0,623	5,4	45,0
Hydro „		51,3	
Thymoquinone	0,579	6,0	43,0
Hydro „		49,0	
Naphtoquinone	0,492	47,5	41,5
Hydro „		89,0	
Antraquinone	0,155	99,0	23,0
Hydro „		122,0	

The values of resonance energies given in col. 2. were calculated from thermochemical data comparing the values of heat of formation with the values of the sum of bond energies. Most of the bond energies were taken from the book of L. PAULING.[3] For the energy of the C—O bond a 20% higher value[4] was used than that given by PAULING. The C = O bond energy value used in these calculations was 16 kcal higher than that given for ketons. This seemed justified since the distance of the C = O bond in quinones[5] and the CO_2 molecule[6] is nearly the same.

Literature.

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