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The π-Bond Energy of the Carbonyl Group

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There exists a large discrepancy in the literature with respect to the π-bond strength of the carbonyl group. From the data compiled by Cottrell[1], figures of 90-93 Kcal/mole for aldehydes and ketones (excluding formaldehyde) are obtained from the differences between their respective double-bond and single-bond energies. In contrast to these high values are the much lower ones of Golden and Benson[2] and of Egger and Cocks[3], 76-78 Kcal/mole. Because of the importance of bond energies in the study of thermochemistry and reaction mechanisms, it would be desirable to reconcile the two sets of numbers.

The latter groups define the π-bond strength as the difference between the O-H bond dissociation energy (BDE) of the alcohol CHR_2OH and the O-H BDE of the radical $\cdot CR_2OH$, reasoning that O-H homolysis in the radical must be assisted by the energy released in the hypothetical reaction $\cdot CR_2O\cdot \longrightarrow CR_2{=}O$. This energy equals the π-bond strength if the C-O bonds in the radical $\cdot CR_2OH$ and the imaginary diradical $\cdot CR_2O\cdot$ are both normal single bonds as in the parent alcohol.

However, the C-O bond in $\cdot CR_2OH$ is not a normal single bond. Radicals of this sort, *i.e.* radicals next to hetero atoms, are stabilized by resonance of the type $\cdot CR_2\text{-}\ddot{O}H \longleftrightarrow {}^{-}CR_2\dot{-}\dot{O}H$, which involves a fractional C-O π-bond[4]. The stabilization energies (SE) of hydroxy- and methoxy-substituted radicals, defined as the difference in BDE's between $H\text{-}CR_2OR$ and $H\text{-}CH_3$ because $CH_3\cdot$ is devoid of all SE of conjugative or hyperconjugative type[5], are 10-14 Kcal/mole[2,6]. This SE, which is absent in the carbonyl compound, must be paid back before calculating the π-bond energy from the O-H BDE of

$\cdot CR_2OH$. When this is done, the 76-78 Kcal/mole figures are raised to about 90 Kcal/mole, and the discrepancy with Cottrell's bond energies all but disappears[7].

Therefore, the best assignment for the π-bond strength of the carbonyl group of aldehydes and ketones at the present time is ca. 90 Kcal/mole.

FOOTNOTES AND REFERENCES

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6 L. F. Loucks and K. J. Laidler, Can. J. Chem., **45**, 2785 (1967); J. A. Kerr, Chem. Rev., **66**, 465 (1966).

7 The argument holds equally well if the C-O π-bond strength were calculated from the difference in BDE's of $H-CR_2OH$ and $H-CR_2O\cdot$, because the former homolysis is assisted by C-O 3-electron bonding, as stated above, while the latter is not, since it gives the carbonyl compound directly.