This Week's Citation Classic™

CC/NUMBER 13
APRIL 1, 1985

Kerr J A. Bond dissociation energies by kinetic methods. *Chem. Rev.* **66**:465-500, 1966.
[Edward Davies Chemical Laboratory, University College of Wales, Aberystwyth, Wales]

The main aim of this review was to present a critical assessment of bond dissociation energies in polyatomic molecules that had been determined by kinetic measurements. A critique of experimental methods was presented, followed by detailed assessments of available data and by tabulated recommended values. [The *SCI*® indicates that this paper has been cited in over 790 publications since 1966.]

J. Alistair Kerr
Department of Chemistry
University of Birmingham
Birmingham B15 2TT
England

February 14, 1985

This review was written while I was a staff member at the University College of Wales, Aberystwyth. The original suggestion to review bond dissociation energies came from my close collaborator at that time, A.F. Trotman-Dickenson. We had both arrived in Aberystwyth in 1960, where we established a large research group in gas kinetics. By 1966, we had completed a series of gas-phase studies of the kinetics of elementary reactions of a range of polyatomic free radicals together with studies of the rates of pyrolyses of organic molecules, all bearing on the general theme of thermochemical kinetics. Shortly before the article was written, Trotman-Dickenson and I had started to contribute a set of tables on bond strengths to the *CRC Handbook of Chemistry and Physics*. We tried hard to keep the tables up-to-date with each annual revision of the handbook, and these tables are still being published and regularly updated.[1] It was a short step to build the review article around the list of bond strengths in polyatomic molecules and the related enthalpies of formation of the corresponding radicals.

I believe that the appeal of the article stems from a number of sources. First, it was timely; there had not been a comprehensive summary of the field for some time before. In addition to the data that we had published at Aberystwyth, other groups had also been active. The studies of S.W. Benson and D.M. Golden at Stanford Research Institute on the reactions of iodine atoms with organic molecules had confirmed a revised set of C-H bond dissociation energies.[2] These and other studies published in the early 1960s established the dominance of kinetic methods of determining bond dissociation energies over methods such as the mass spectrometric approach. This has been further confirmed since the publication of the review article by the development of yet another important kinetic method, namely, the very low pressure pyrolysis technique of Benson.[3]

Other features that I feel helped to make this article a *Citation Classic* include the attempt to make the review both critical and comprehensive. In addition, I am convinced that publication in *Chemical Reviews*, with its high reputation and wide circulation, considerably enhanced the number of citations.

I well remember the thrill that I received, as a relatively young scientist, at the pile of reprint cards that flooded in for this article (it was the pre-Xerox age!). I still receive the occasional request for a reprint despite the publication of a number of subsequent reviews.[3-6] The citation success that this article has achieved strengthens my belief that writing critical reviews can be a worthwhile and rewarding exercise.

1. **Kerr J A.** Strengths of chemical bonds. (Weast R C. ed.) *CRC handbook of chemistry and physics*. Boca Raton. FL: CRC Press, 1985. p. F171-90.
2. **Golden D M & Benson S W.** Free-radical and molecule thermochemistry from studies of gas-phase iodine-atom reactions. *Chem. Rev.* **69**:125-34, 1969. (Cited 300 times.)
3. **McMillen D R & Golden D M.** Hydrocarbon bond dissociation energies. *Annu. Rev. Phys. Chem.* **33**:493-532, 1982.
4. **Egger K W & Cocks A T.** Homopolar and heteropolar bond dissociation energies and heats of formation of radicals and ions in the gas phase. I. Data on organic molecules. *Helv. Chim. Acta* **56**:1516-36, 1973. (Cited 150 times.)
5. **Walsh R.** Bond dissociation energy values in silicon-containing compounds and some of their implications. *Account. Chem. Res.* **14**:246-52, 1981.
6. **Rodgers A S.** Thermochemistry of fluorocarbon radicals. *ACS Symp. Ser.* **66**:296-313, 1978.