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# **Explaining C-H Bond Strengths**

### Alternative to hyperconjugation invokes steric strain, but not everyone is buying the idea

#### Elizabeth K. Wilson



Courtesy of Scott Gronert

**Repulsive** Gronert's explanation for the variation in stabilities of C–H bonds in alkanes, shown in this cartoon, invokes repulsive forces (represented by the red springs) between atoms attached to the same atom. When a C–H bond breaks, the springs and

## associated strain energy are released.

From their first organic chemistry course, students learn that the more substituted an alkane, the weaker the remaining C-H bonds, and the more stable the molecule's corresponding radical. The reason for these variations in bond strengths is so well-accepted that few chemical educators give it much thought.

That explanation is hyperconjugation, in which hybrid orbitals on a neighboring C-H or C-C bond overlap with a singly occupied p orbital on the central carbon, thereby delocalizing electrons and thus increasing the radical's stability.

But how do chemists know that that's really what's going on? Though they can measure bond dissociation energies, hyperconjugation itself can't be directly observed.

It can be inferred from some experimental results, such as electron spin resonance spectra, and many chemists point to a great deal of theoretical evidence that supports it. In addition to bond strengths, hyperconjugation neatly explains a host of other properties, from the gauche effect to ethane rotation. So why mess with it?

For a handful of chemists, hyperconjugation has some shortcomings they just can't reconcile. For example, although C-H bond dissociation energies decrease as alkane systems become more substituted, systems involving bonds between carbon and other atoms, such as halogens, do not. "This is something we've known for a long time, but it is literally ignored in most textbooks," says <u>Robert G. Bergman</u>, a chemistry professor at the University of California, Berkeley.

These different trends imply that some other effect-involving interactions in the parent molecule and not just hyperconjugation in the radical-must be at work.

Scott Gronert, a chemistry professor at San Francisco State University, has now proposed a different scenario to explain the variations in alkane C-H bond strengths. In a simple fashion, and without invoking hyperconjugation, he argues that as more substituents are added onto a central carbon, and the bulkier they become, the more these groups will want to get out of each other's way.

More precisely, Gronert says, C-H bonds are weakened by the steric strain between two atoms or alkyl groups that are attached to the same carbon atom, a phenomenon he calls "geminal" repulsion. And when a C-H bond is broken, the release of the strain is what leads to lower bond dissociation energies, he believes. Gronert says he doesn't dismiss hyperconjugation altogether, but he doesn't believe it's responsible for the effects in this case.

Though hyperconjugation has largely reigned supreme since it was proposed by Nobel Laureate Robert S. Mulliken in the 1930s, the idea that steric strain affects bond stability isn't new. Gronert himsel discovered a 1932 *Journal of the American Chemical Society* paper by noted theoretical chemist Henry Eyring that suggests that very notion. Others, such as emeriti chemistry professors Lawrence S. Bartell, at the University of Michigan, and Kenneth B. Wiberg, at Yale University, also have advocated the importance of repulsive interactions in molecular geometries during their careers.

Gronert has devised an empirical model, based on the number and types of geminal interactions, to calculate the heats of formation of alkanes and their radicals. The calculated values, and the corresponding bond dissociation energies, closely match experimental values (*J. Org. Chem.* **2006**, *71*, 1209). It's a somewhat heterodox idea that Gronert hopes will stir up discussion among his theoretical organic chemist colleagues.

And create a stir it has.

"The work is a breath of fresh air in that it forces us to think about reasons for fundamental chemical facts," says theoretical organic chemist <u>Andreas A. Zavitsas</u> at Long Island University, in Brooklyn.

"I have, for a long time, been convinced that hyperconjugation was not the explanation for the differences in alkyl radical stabilities," Wiberg says.

Others, however, aren't convinced at all. "The fact that Gronert's set

of parameters can reproduce the energies of a limited number of hydrocarbons does not prove the validity of his assumptions," says <u>Paul v. R. Schleyer</u>, chemistry professor at the University of Georgia, Athens. "He does not consider the vast modern theoretical and computational support for hyperconjugation."

Weston T. Borden, chair of the chemistry department at the University of North Texas in Denton, is also wary. "The danger in drawing a conclusion about physics from any empirical fitting scheme is that a fortuitous cancellation of errors can lead to a successful fit while ignoring physical effects that may actually be present," he says.

"Replacing an explanation based on sound quantum mechanics with a numerical correlation seems like a step backward," agrees <u>Kendall N. Houk</u>, a chemistry professor at UCLA.

But chemistry professor <u>Barry K. Carpenter</u> of Cornell University acknowledges some of the limitations of hyperconjugation. "I think Scott is making some important points," he says. "But finding a definitive answer to what is responsible for bond energies is likely to be tough."

Andrew Streitwieser, emeritus chemistry professor at UC Berkeley, under whom Gronert got his Ph.D., comments that chemists who think about this problem will be enriched by considering both interpretations. "We'll end up with a better understanding that we'll be teaching to undergraduates in the future," he says.

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