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Letters

More charge

I should like to congratulate Ms. Garmon on an excellent piece of scientific journalism ("The Disputed Charge Account," SN: 8/12/83, p. 106). However, her account omits one crucial point, and also gives an unclear explanation of one of the principal pieces of evidence.

No one—not even H.C. Brown himself!—disputes that many carbocations in the gas phase have delocalized charge distribution, with two or more carbon atoms sharing the plus charge. H.C. Brown is talking about reaction conditions, in solvents where there are atoms with non-bonding electron pairs available to stabilize the positive charge on one carbon atom. This is what happens when the carbocation reacts to form products—and no one argues about this, either. So the argument comes down to whether, in cation-stabilizing solvents, the 2-norbornyl cation is produced in the delocalized form and then gets perturbed by the solvent into the "classical" carbocation with localized plus charge as the first step towards bond formation,

This Week

- 276 Electrons Fly as Computer Chess Champ Crowned
- 276 Nuclear accident that kills one is attributed to human error
- 276 Three guilty of fraud
- 277 Venera 15 and 16 at work: A factor in U.S. Venus plans?
- 277 Sun's dust rings confirmed
- 278 Star works receive physics Nobel
- 278 Inorganic chemist wins Nobel Prize
- 278 How to enlighten computer logic
- 279 Garden home remedies give mixed results
- 279 The pill revisited: New cancer link?

Research Notes

- 280 Earth Sciences
- 281 Physical Sciences
- 281 Nutrition

Articles

282 A Computer-Generated Cosmic Portfolio

Cover: Just how large, lumpy collections of galaxies, such as the Coma Cluster shown on the cover, could have evolved from a smooth, young universe remains a mystery to cosmologists. The dark matter now binding the cluster together may also have been the prime mover in its formation. (Photo © 1973 AURA, Inc., Kitt Peak National Observatory)



Departments

275 Letters

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or whether it gets produced directly in the solvent-stabilized classical form, which has to gain energy in order to throw off the solvent molecule and rearrange. Many chemists do not consider this question of world-shaking importance.

Now the methods described for determining carbocation structure require a stable cation in solution, which by definition means that the solvent interaction cannot be strong enough to lead to bond formation. It is now clear that in such solvents the 2-norbornyl cation is more stable in a delocalized structure. The account of "Saunders' Method" for determining this needs clarification. The position of the carbon-13 NMR peak is greatly affected by whether the carbon atom carries a positive charge. In such an equilibrating mixture where the two carbon atoms which alternate having the plus charge are identically substituted, each will have the plus charge half of the time, and if the equilibration is rapid enough, each will give the same NMR carbon-13 signal halfway between the C+ and neutral C positions. Saunders had the brilliant idea (this is a little different from a "discovery") of substituting deuterium next to one

of the two carbons referred to. This makes it less stable as a carbocation, so it spends less time with the plus charge and the other carbon spends more. The result is that you get two carbon-13 peaks widely separated. If however you have a molecule permanently in the "halfway between" state, then deuterium substitution will have only a small effect on the C-13 NMR signal, and you see two closely spaced peaks. Saunders and co-workers first demonstrated this with several different types of carbocations, and then applied the technique to the 2-norbornyl cation.

Neil McKelvie
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Corrections:

In "In a Ferment" (SN: 10/8/83, p. 234), the reduction Clyde got in fermentation time was 150 fold, or 15,000 percent, not 150 percent.

In "Playing Chess Bit by Bit" (SN: 10/8/83, p. 236), the man on the left in the computer chess photo on p. 237 is Joseph Condon.

OCTOBER 29, 1983

275