THE RELATIVE RATES OF ELECTRON-RICH AND ELECTRON-DEFICIENT ALKENE CYCLOADDITIONS TO BENZYNE.
ENHANCED ELECTROPHILICITY AS A CONSEQUENCE OF ALKYNE BENDING DISTORTIONS.

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Abstract: Benzyne reacts more rapidly with electron-rich alkenes than electron-deficient alkenes, a result of the abnormally low energy LUMO of benzyne, which results from the acetylene bending enforced by the benzyne geometry.

Although benzyne has been characterized as an electrophilic species,[2] we are aware of no attempts to explain in detail why the electrophilic character of this highly distorted acetylene should be enhanced more than its nucleophilic character.[3] In the course of our theoretical investigations of nucleophilic additions to acetylenes,[4] we have found that the well-known electrophilicity of benzyne is a result of the bending of the alkyne moiety, which lowers the alkyne LUMO with respect to that of an unstrained alkyne, but has little effect on the HOMO. We also report experimental rates of [2 + 2] cycloadditions of a series of alkenes to benzyne, which reinforce the generalization that the electrophilic reactivity of benzyne is enhanced more than the nucleophilic reactivity as compared to that of unstrained acetylenes.

Figure 1 shows the frontier molecular orbitals of 2-butyne and various distorted 2-butyne models which mimic angle and bond length distortions present in benzyne. The orbitals were obtained by ab initio calculations, using the 4-31G basis set.[5] The calculations shown for benzyne are based on the geometry reported by Berry et al.[6] Recently ab initio (STO-3G and 4-31G)[7] and semiempirical[8] calculations indicate that the formal triple bond length is very similar to that of an unstrained acetylene,[9] but this will not change any of the arguments made here.

The benzyne SHOMO[10] and LUMO are very similar in shape and energy to the HOMO and LUMO of 2-butyne distorted so that the carbon skeleton has the same geometry as $C_6 C_1 C_2 C_3$ of benzyne. Although vacant orbitals calculated in this way are much too high in energy, the changes in orbital energies upon distortion should be reproduced fairly well.[4]

The most notable effect on orbital energies arises upon bending of the 2-butyne. This dramatically lowers the LUMO but has a very small effect on the HOMO.[4,11] We have shown that
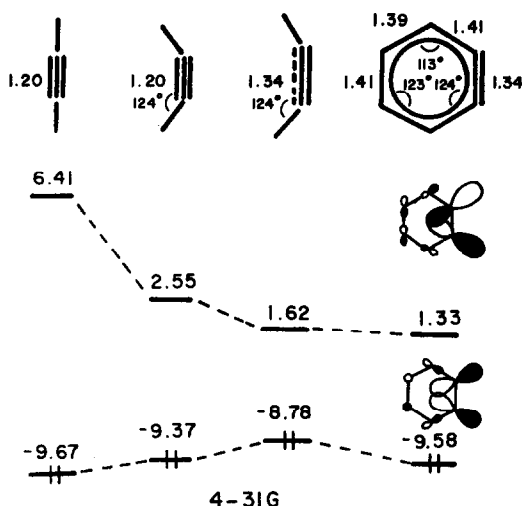
FIGURE 1. FRONTIER ORBITALS AND ENERGIES (eV) FOR 2-BUTYNE MODELS AND BENZYNE.

this arises from the efficient mixing of the π^* orbital with a σ^* orbital which lies only slightly higher in energy. Stretching lowers the LUMO and raises the HOMO slightly, further compressing the HOMO-LUMO gap.[8] The LUMO of benzyne has mixed in some s character (each diagonal carbon is "sp[15]"), while the SHOMO is composed of pure, but tilted, p orbitals. This description is rather different from previous theoretical descriptions,[9,12] which generally picture these orbitals as composed of hybrids with appreciable s character.

The very low energy of the benzyne LUMO, and rather ordinary energy of the HOMO, account for the electrophilic nature of benzyne.[2,13] That is, the LUMO will interact much more strongly than that of an undistorted acetylene with the HOMO of a nucleophile, while the benzyne HOMO-electrophile LUMO interaction will be quite normal.

There are several experimental indications of the electrophilicity of benzyne.[2] For example, in Diels-Alder reactions with anthracenes, benzyne tends to attack the more electron-rich benzene ring.[14] In competitive reactions between ethanol and halides, benzyne behaves as "soft" electrophile, reacting in the order: $I^- > Br^- > Cl^-$.[2,15]

A direct comparison of the relative electrophilicity and nucleophilicity of benzyne results from our measurements of the relative rates of [2 + 2] cycloadditions of benzyne to electron-rich and electron-deficient alkenes, summarized in Table 1. The formation of the benzocyclobutenes occurs through a stepwise mechanism, since the reactions are non-stereospecific.[16] The rates were measured by a competitive technique, from the equation:

$$\frac{k_a}{k_b} = \frac{[P_a]}{[P_b]} \times \frac{[B]}{[A]} ,$$

where [B]/[A] is the ratio of concentrations of alkenes, A and B, and $[P_a]/[P_b]$ is the ratio of benzocyclobutenes formed in the reaction, determined by vpc. The values of k_{rel} were checked using several pairs of alkenes to determine each relative rate constant. Benzyne was generated by the thermal decomposition of benzenediazonium-2-carboxylate hydrochloride.[17]

To be completely candid, we show a plot of log k_{rel} versus the alkene vertical ionization potentials in Figure 2. This plot obviously does not give a linear relationship! This is

Table 1. Relative Reactivities of Alkenes ($CH_2=CR_1R_2$) Towards Benzyne.

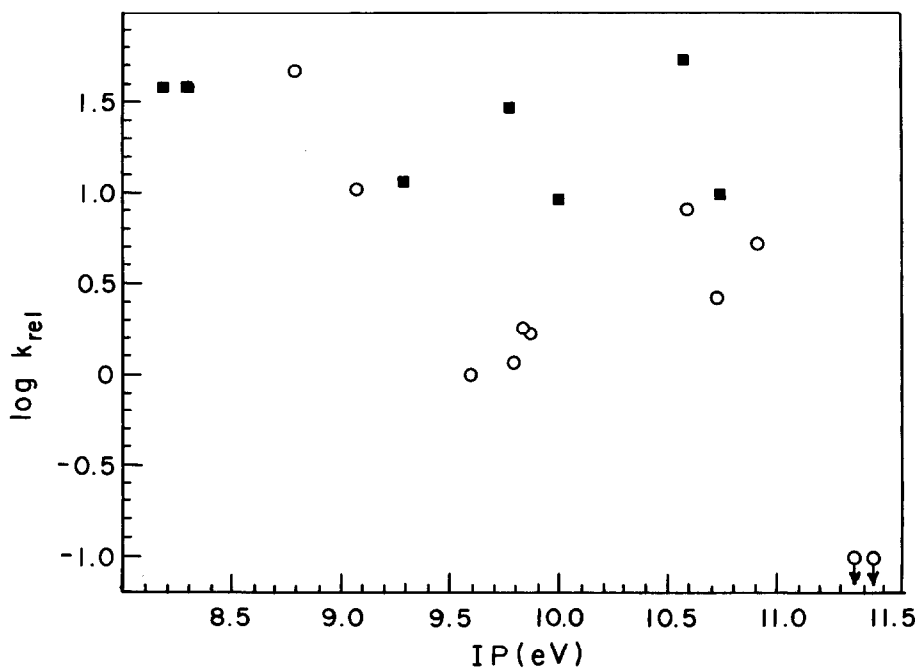| R_1	R_2	IP(eV)	k_{rel}
t-Bu-	MeO-	8.2(est.)	38.9
EtO-	EtO	8.30	38.9
c-MeCH=CH-	H-	8.78	46.5
EtO-	H-	9.07	10.5
t-Bu-	Cl-	9.3	11.6
t-Bu-	H-	9.61	1.0
Br-	Br-	9.78	30.2
Me_3Si-	H-	9.8	1.16
AcO-	H-	9.85	1.79
Br-	H-	9.87	1.75
Cl-	Cl-	10.00	9.42
Cl-	NC-	10.58	54.1
MeCO-	H-	10.60	7.88
MeO_2C-	H-	10.72	2.72
AcO-	NC-	10.76	9.57
NC-	H-	10.92	5.25
O_2N-	H-	11.38	<0.1
$H_2C=CHSO_2-$	H-	11.45	<0.1

FIGURE 2. PLOT OF RATES VERSUS IPS.
Open Circles = Monosubstituted Alkenes; Squares = 1,1-Disubstituted Alkenes.

probably due to the wide variety of alkenes studied. However, there seems to be a trend toward higher reactivity with decreasing IP (i.e., increasing nucleophilicity) of the alkene, and, most importantly, very electron-deficient alkenes cannot compete with the dimerization of benzyne.

This suggests that benzyne itself is even more electrophilic than the last two alkenes in Table 1, in qualitative accord with theoretical expectation.

In summary, the bent triple bond of acetylene confers abnormally high electrophilic character on benzyne, the result of large LUMO stabilization upon bending.

REFERENCES AND NOTES

1. (a) Present address: Department of Chemistry, University of Nebraska-Omaha, Omaha, Nebraska 68108; (b) Taken in part from Ph.D. Dissertation of A. T. Bowne, Harvard University, 1975; (c) Present Address: IBM Office Products Division, Boulder, Colorado 80302.

2. (a) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, 1967; (b) R. W. Hoffmann in G. G. Viehe, Ed., "Chemistry of Acetylenes", Marcel Dekker, New York, 1969, Chapter 16; (c) W. J. leNoble, "Highlights of Organic Chemistry", Marcel Dekker, New York, 1974, Chapter 19.

3. S. Inagaki and K. Fukui, Bull. Chem. Soc. Japan, 46, 2240 (1973) have noted that the LUMO of benzyne obtained from an ab initio calculation (D. L. Wilhite and J. L. Whitten, J. Am. Chem. Soc., 93, 2858 (1971).) is very low in energy.

4. R. W. Strozier, P. Caramella, and K. N. Houk, J. Am. Chem. Soc., 101, 1340 (1979).

5. R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys., 54, 724 (1972).

6. J. W. Laing and R. S. Berry, J. Am. Chem. Soc., 98, 660 (1976). The angles at C_3, C_4, C_5, and C_6 were adjusted to give an internally consistent structure.

7. M. D. Newton and H. A. Frankel, Chem. Phys. Lett., 18, 244 (1973).

8. K. Yamaguchi, A. Nishio, S. Yabushita, and T. Fueno, Chem. Phys. Lett., 53, 109 (1978).

9. For the most recent calculations on benzynes, see J. O. Noell and M. D. Newton, J. Am. Chem. Soc., 101, 51 (1979).

10. The HOMO is at -9.35eV and is a π orbital.

11. S. Y. Chu and L. Goodman, J. Am. Chem. Soc., 97, 7 (1975).

12. R. Hoffmann, A. Imamura, and W. J. Hehre, J. Am. Chem. Soc., 90, 1499 (1968).

13. Making the usual corrections to the 4-31G energies, we can estimate the SHOMO ionization potential to be about 9.5eV, essentially the same as the IP (9.56eV) of 2-butyne (P. Carlier, J. E. Dubois, P. Masclet, and G. Mouvier, J. Electron Spectrosc., 7, 55 (1975).), and the LUMO electron affinity to be about 2.5eV, similar to that of tetracyanoethylene (2.9eV), see K. N. Houk and L. L. Munchausen, J. Am. Chem. Soc., 98, 937 (1976) and references therein.

14. B. H. Klanderman, J. Am. Chem. Soc., 87, 4649 (1965).

15. R. W. Hoffmann, G. E. Vargas-Nunez, G. Guhn, and W. Sieber, Chem. Ber., 98, 2074 (1965).

16. M. Jones, Jr. and R. H. Levin, J. Am. Chem. Soc., 91, 6411 (1969); P. G. Gassmann and H. P. Benecke, Tetrahedron Lett., 1089 (1969) and references therein.

17. D. C. Dittmer and E. S. Whitman, J. Org. Chem., 34, 2004 (1969).