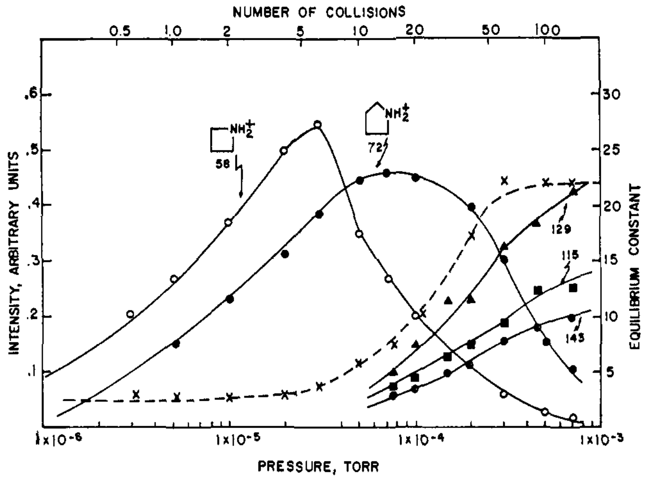

Figure 1. Relative ion intensities *vs.* pressure of the product ions in a 5.1:1.0 mixture of $(CH_2)_3NH$ and $(CH_2)_4NH$ at 9 eV. The protonated species (*m/e* 58, 72) were formed by proton transfer from the parent ions (*m/e* 57, 71) to the two neutral molecules. The dashed line denotes $K = [(CH_2)_4NH_2^+][(CH_2)_3NH]/[(CH_2)_3NH_2^+][(CH_2)_4NH]$. The number of collisions was approximated from the orbiting limit. *K* was determined directly from the ionic intensities without mass correction.

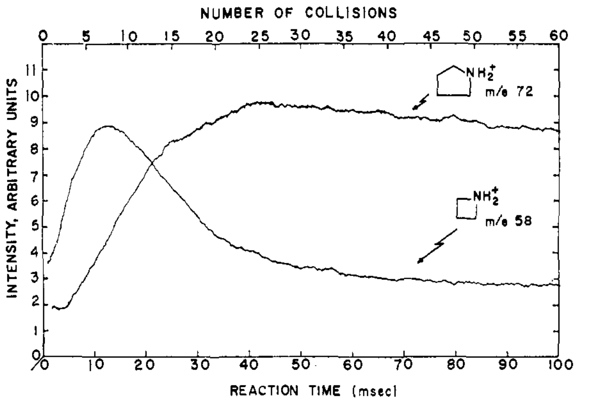

Figure 2. Pulsed icr data for the $(CH_2)_3NH_2^+$ and $(CH_2)_4NH_2^+$ peaks in a 6.4:1.0 mixture of $(CH_2)_3NH$ and $(CH_2)_4NH$ at 10 eV and approximately 1×10^{-5} Torr. The protonated species (*m/e* 58, 72) were formed by proton transfer from the parent ions (*m/e* 57, 71) to the two neutral molecules. Each measured ionic intensity was multiplied by the mass of the ion to obtain *K*.

lapping data provide free energies with an uncertainty of less than ±0.2 kcal/mol.[8]

At high pressures, collision-stabilized proton-bound dimers (*m/e* 115, 129, 143) are formed (Figure 1). These dimers rapidly come to equilibrium and the resulting equilibrium constants directly yield quantitative relative stabilities of the dimers.[9]

Concern that the formation of the proton-bound dimers might affect the equilibrium between the protonated parent ions led us to perform experiments on the same mixtures using a pulsed ion cyclotron resonance spectrometer fitted with a trapped ion analyzer cell.[10] With this new technique, gaseous ions are formed by a short pulse of an electron beam and then trapped within the analyzer cell for times variable from 1 to 500 msec. As the ions react with the neutral molecules, the abundance of each mass ion can be monitored as a function of the reaction time. At pressures below 10^{-5} Torr the proton-bound dimers are not observed because the time between collisions is long relative to the lifetime of the unstabilized proton-bound dimer. For the pulsed icr experiments equilibrium was studied by trapping the ions for reaction times of 100 msec at low pressures. A typical experiment is shown in Figure 2 for a mixture of azetidine (**4**) and pyrrolidine (**3**). Equilibrium is reached in about 40 collisions with a $\Delta G^{25°}$ of 1.9 ± 0.1 kcal/mol. Each determination of ΔG by the high-pressure technique was confirmed (±0.1 kcal) by the pulsed icr technique.

Accurate relative proton affinities are very useful in correlation with chemical reactivity, solution basicity, structure, molecular orbital calculations, and other physical data. We have examined some of these correlations for a large number of amine proton affinities determined by this technique.[11] The scope of the technique for proton affinities of other classes of molecules and for equilibrium studies in a variety of other gas phase reactions is also under investigation.

Acknowledgment. The authors wish to thank Professor John D. Baldeschwieler for reading the manuscript and offering several helpful suggestions.

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[8] The runs were done on several different neutral mixtures at high observing frequency and long drift times to ensure minimal differential pumping or adsorption effects.

[9] D. H. Aue, H. M. Webb, and M. T. Bowers, details to be published. Similar equilibria have been observed in a high-pressure mass spectral study of ammonia, water, and methanol: S. K. Searles and P. Kebarle, *J. Phys. Chem.*, **72**, 742 (1968), and references therein.

[10] R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); K. C. Smyth, R. T. McIver, Jr., J. I. Brauman, and R. W. Wallace, *J. Chem. Phys.*, in press; R. T. McIver, Jr., and M. A. Haney, submitted for publication.

[11] D. H. Aue, H. M. Webb, and M. T. Bowers, manuscript in preparation.

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Received April 12, 1971

Alkyl Substituent Effects on Gas-Phase Acidities. The Influence of Hybridization

Sir:

The problem of the effect of alkyl substituents on reaction rates and equilibria continues to be a vexing one.[1] We have shown previously that in the gas phase, in saturated systems, alkyl groups appear to stabilize both positive and negative charges, in accordance with a polarization stabilization mechanism.[2,3] In general, for those systems thus far examined, the dipole moment associated with the varying alkyl portion of the molecule would be expected to be small and fairly constant in a given series. Thus, replacing a hydrogen with methyl in the parent saturated system simply increases

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[1] For example, see M. J. S. Dewar, *Tetrahedron*, **17**, 123 (1962); P. von R. Schleyer and C. W. Woodworth, *J. Amer. Chem. Soc.*, **90**, 6528 (1968), and references cited therein. Also, see E. M. Arnett and J. W. Larsen, *ibid.*, **91**, 1438 (1969); W. M. Schubert and D. F. Gurka, *ibid.*, **91**, 1443 (1969); A. Himoe and L. M. Stock, *ibid.*, **91**, 1452 (1969).

[2] J. I. Brauman and L. K. Blair, *ibid.*, **92**, 5986 (1970); **90**, 6561 (1968).

[3] J. I. Brauman and L. K. Blair, *ibid.*, **93**, 3911 (1971); **91**, 2126 (1969); J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971).

the polarizability without changing the dipole moment appreciably.

The only available data on the effect of alkyl groups in unsaturated systems suggest that alkyl groups bonded to unsaturated (sp or sp^2) carbon are electron releasing relative to hydrogen. These include, for example, dipole moments in toluene and methylacetylene[4] and measurements in solution in which para methyl appears to destabilize benzyl,[5] phenoxide, and benzoate anions.[6] Having previously established that gas-phase stability orders are often reversed from those in solution,[2,3] we thought it would be of value to explore the effect on acidity of alkyl groups bonded to trigonal and digonal carbon. In this communication we describe some results on the relative acidities of toluene and *p*-xylene and acetylene and substituted acetylenes, as determined by ion cyclotron resonance (icr) spectroscopy.

Experiments were carried out as described previously,[2,3] and acidity orders are inferred from the observation of the preferred direction of a reaction. We find the acidity orders ethanol > toluene > methanol > *p*-xylene > water, and acetylene > *n*-butylacetylene > methylacetylene > water.[7] Thus, in systems involving bonding to unsaturated carbon, alkyl groups relative to hydrogen appear to destabilize anions in the gas phase. Nevertheless, in accord with our observations in other systems, larger alkyl groups are stabilizing relative to smaller ones. These experimental observations are thus partially accommodated by the usual inductive picture of alkyl substituent effects, the unsaturated carbon being more electronegative, withdrawing electrons from the polarizable alkyl group, and so giving rise to a group dipole.[9,10] This dipole, then, oriented toward the localized negative charge in the anion, destabilizes the system. However, the group dipole is relatively insensitive to the size of the alkyl group,[4] so this dipolar term remains constant as the alkyl size increases. Meanwhile the larger alkyl group is more polarizable, and thus more stabilizing than a small one. Consequently, more highly substituted acetylenes are more acidic.

CNDO/2 Calculations. Because most calculations of molecule and ion stabilities refer to the isolated species, it is difficult, if not impossible, to compare the results of calculations with chemical behavior in solution. However, our gas-phase acidity orders are ideally suited for testing theory, since the species involved are precisely those whose properties are calculated. Our previous experimental results have given rise to a substantial number of calculations, both *ab initio*[11] and semiempirical,[12] all of which have confirmed our results. It has been pointed out by Jesaitis and Streitwieser[13] that some of this agreement may be fortuitous, inasmuch as certain calculations disagree with experiments, albeit in solution. We have utilized the CNDO/2 method[14] to calculate the relative acidities of acetylene and alkylacetylenes and find a predicted order of ethylacetylene > methylacetylene, but methylacetylene > acetylene in disagreement with experiment. Our experimental finding that toluene > *p*-xylene is also at variance with the CNDO/2 calculations of Streitwieser, *et al.*[15] Furthermore, the interrelationship between types of compounds is predicted badly. We calculate, for example, water > acetylene, also in disagreement with experiment.

Thus, we concur that the CNDO/2 method should only be used circumspectly, if at all, for predicting anion stabilities.[15] The reasons for the failure of this and possibly all Hartree–Fock SCF methods[11b] for calculating anion stabilities doubtless lie in the electron correlation problem, which is expected to be especially severe for negatively charged systems. Consequently, we believe that previous agreement between calculated and experimental acidity orders should probably be viewed as fortuitous until a more rigorous basis for the success (or failure) of the calculations is established.

Acknowledgment. We thank Professor J. D. Baldeschwieler for his support, J. V. Garcia for technical assistance, and Professor L. J. Altman for advice and discussions regarding the calculations. This work was supported by the National Science Foundation (GP-27532, GP-23406), the National Aeronautics and Space Administration (NGL-05-020-250), the National Institutes of Health (GM-14752), and the Center for Materials Research Stanford University.

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(4) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

(5) A. Streitwieser, Jr., and H. F. Koch, *J. Amer. Chem. Soc.*, **86**, 404 (1964).

(6) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 142.

(7) Equilibrium acidities in solution have been determined for only a small number of acetylenes.[8] In solution acetylenes appear to be substantially less acidic than water.

(8) For recent work and references, see A. Streitwieser, Jr., and D. M. E. Reuben, *J. Amer. Chem. Soc.*, **93**, 1794 (1971).

(9) See, for example, M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

(10) However, for a different view of the origin in the dipole moment of methylacetylene see (a) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967); (b) M. D. Newton and W. N. Lipscomb, *ibid.*, **89**, 4261 (1967).

(11) (a) W. J. Hehre and J. A. Pople, *Tetrahedron Lett.*, 2959 (1970); (b) P. H. Owens, R. A. Wolf, and A. Streitwieser, Jr., *ibid.*, 3385 (1970).

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(13) R. G. Jesaitis and A. Streitwieser, Jr., *Theoret. Chim. Acta*, **17**, 165 (1970).

(14) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970. "Standard geometries" were used; the calculations were carried out using the program CNINDO detailed in the book and obtained from Quantum Chemistry Program Exchange.

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(16) (a) Alfred P. Sloan Fellow; (b) National Science Foundation Predoctoral Fellow, 1966–1970.

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Received May 17, 1971

A New Synthesis of Olefins

Sir:

We describe a new and general synthesis of tetrasubstituted olefins noteworthy for its simplicity and for producing pure products in high yields. Both symmetrical and unsymmetrical olefins are readily obtained.

In this synthesis aliphatic nitro compounds[1] are

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(1) These are readily available commercially, or by a variety of well worked out procedures: *cf.* N. Kornblum, *Org. React.*, **12**, 101 (1962).