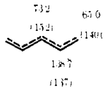
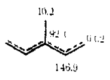
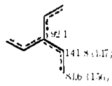
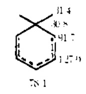
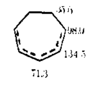
Delocalized Carbanions. Carbon Nuclear Magnetic Resonance Spectra, Charge Distribution, and Reaction Sites

Sir:

Although cmr chemical shifts have been reported for many delocalized carbonium ions[1,2] and provide the best measure of the electron density distribution in such ions,[3] shifts have not yet been reported for the corresponding anions. We wish to record cmr parameters and reaction sites for several delocalized carbanions, and to discuss their relation to charge distribution in the anions.

Our results and some earlier reactivity data are given in Table I. Chemical shifts were measured directly on natural abundance samples using Fourier Transform (FT) spectrometry.[4] The ^{13}C–H coupling constants were obtained by finding ^{13}C satellites in the pmr spectrum, and in the cases where the satellites were found, the ^{13}C shift assignments were verified by the indor method.[5]

Table I. Cmr Shifts, ^{13}C-H Coupling Constants, and Reaction Sites for Some Delocalized Carbanions

	Anion[a]	% of reaction at central atom with Water	 Methyl iodide	 Ethylene oxide
I		10[b]	35	65[c]
II[d]				
III[e]				77[c]
IV		60[b]	100	
V		25[f]		100
VI[g]		50	100	100

[a] With cmr shifts in ppm from TMS, and in parentheses, ^{13}C-H coupling constants in Hz. [b] R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 199 (1967). [c] J. G. Berger, E. L. Stogryn, and A. A. Zimmerman, *J. Org. Chem.*, **29**, 950 (1964). [d] Prepared in the usual way[b] from 3-methyl-1,4-pentadiene purchased from Chemical Samples Co. [e] R. B. Bates, S. Brenner, and C. M. Cole, *J. Amer. Chem. Soc.*, **94**, 2130 (1972). [f] R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *ibid.*, **91**, 4608 (1969). [g] R. B. Bates and D. A. McCombs, *Tetrahedron Lett.*, 977 (1969).

The most striking feature of the spectra is that the *odd-numbered carbons* in all of the pentadienyl and 3-vinylpentadienyl systems all *absorb at higher field* (65–99 ppm) *than the even-numbered carbons* (127–147); this finding, opposite from that with delocalized carbonium ions,[1,2] is in accord with expectation from MO theory.[6] The ranges for even-numbered carbons overlap with those of alkenes (105–150)[7] and the even-numbered carbons in the corresponding carbonium ions (133–137),[1,2] indicating that *very little of the charge density in the cations and anions is located on the even-numbered atoms*, again in agreement with MO theory.[6] The absorption of the even-numbered atoms in the pentadienyl system of IV at higher field than the even-numbered atoms in the other anions is possibly due to homoconjugation in this cyclohexadienyl system,[8] and possibly simply to γ-shielding effects.[4]

In the absence of bond-length measurements on delocalized carbanions, MO calculations do not answer the more subtle question of charge distribution among the odd-numbered carbons in an anion such as pentadienyl (I); greater density at the center or ends can be calculated, depending on the carbon–carbon bond lengths chosen. In the cmr spectra, the central atom of the conjugated system absorbs farther *downfield* in the *acyclic* anions I–III and farther *upfield* in the *cyclic* anions IV and V. Interpretation of these findings is complicated by possible homoconjugation in the cyclic anion IV (see above) and by the different degrees of alkyl substitution at the odd-numbered atoms in the various anions (the usual order of shift to higher field for carbons is tertiary > secondary > primary.[9] This latter effect can be seen by comparing the shifts in I and II: in II, the central atom is tertiary instead of secondary and is shifted downfield by 18.9 ppm, whereas the end carbons each absorb 0.8 ppm farther upfield.[10] The effect of substituting alkyl groups for hydrogens may be largely due to the removal of electronic charge;[1] if so, the sp^2 carbons absorbing farther upfield in anions I–V probably do bear greater charge density. The terminal carbons in III presumably absorb at lower field than those in I and II because the charge is delocalized over more atoms in the former.

It was postulated long ago that cyclohexadienyl anions, the last intermediates in the Birch reduction of aromatics to 1,4-cyclohexadienes, protonate faster at the central atom of the pentadienyl system than at the ends.[11] The results of some presumably kinetically controlled reactions of several delocalized anions are

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(1) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(2) G. A. Olah and R. D. Porter, *ibid.*, **93**, 6877 (1971).

(3) There have been many successful correlations of electron density with pmr and cmr shifts, but as protons are one bond removed from the carbon whose charge is of interest and are much more susceptible to other influences, carbon shifts must provide a better measure of electron distribution in carbonium ions and carbanions. Cmr shifts have a special advantage in cases in which a charged atom bears no hydrogen, as in II and III.

(4) The FT cmr spectra were run on THF–hexane solutions and calibrated using the upfield hexane peak, assumed to be 12.3 ppm downfield from TMS: D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964).

(5) E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962); G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Amer. Chem. Soc.*, **85**, 1328 (1963).

(6) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(7) R. K. Jensen and L. Petrakis, *J. Magn. Resonance*, **6**, 105 (1972).

(8) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Amer. Chem. Soc.*, **85**, 3031 (1963); R. B. Bates, E. S. Caldwell, and H. P. Klein, *J. Org. Chem.*, **34**, 2615 (1969).

(9) E. Breitmaier, G. Jung, and W. Voelter, *Angew. Chem., Int. Ed. Engl.*, **10**, 679 (1971).

(10) *Cf.* the downfield shift of 25 ppm at the central atom and 3 ppm at each end atom caused by adding a methyl group to the central carbon in the ethylbenzenium ion, a *carbonium* ion.[2]

(11) A. J. Birch, *Quart. Rev., Chem. Soc.*, **4**, 69 (1950).

given in Table I. In these anions, as in allylic anions[11,12] and enolates,[13] one finds some correlation between the favored reaction site and the carbon of greatest electron density, for *in the cyclic anions* IV–VI, *more reaction occurs at the central atom than in the acyclic anions* I and III. Electron density is certainly not the sole factor governing reaction site in these anions,[14] but the above correlation suggests its involvement.

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[12] D. E. O'Connor and C. D. Broaddus, *J. Amer. Chem. Soc.*, **86**, 2267 (1964).

[13] L. S. Melvin, Jr., and B. M. Trost, *ibid.*, **94**, 1790 (1972).

[14] The principle of least motion has been invoked by J. Hine, *J. Org. Chem.*, **31**, 1236 (1966), to explain the higher reactivity of cyclohexadienyl anions at the central atom.

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Homogeneous Catalysis of a Gas-Phase, Ion–Molecule Reaction

Sir:

In contrast to the general observation that many exothermic ion–molecule reactions exhibit similar rate constants and have no activation energy,[1a] we have observed that gas-phase proton-transfer reactions involving highly delocalized anions (*viz.* benzyl, allyl, enolates, etc.) appear to be unusually slow.[1b] This phenomenon is accentuated when both reactant and product are resonance stabilized. Indeed, we have not been able to observe certain proton transfers, which are known to be exothermic, by the usual ion cyclotron resonance (icr) double resonance technique.[2] For example, while reactions 1 and 2 are observable, 3 does not appear to occur on the normal double resonance time scale.[3a]

$$CH_3OH + CH_2{=}CHCH_2^- \xrightarrow{k_1} CH_3O^- + CH_3CH{=}CH_2 \quad (1)$$

$$C_6H_5CH_3 + CH_3O^- \xrightarrow{k_2} C_6H_5CH_2^- + CH_3OH \quad (2)$$

$$C_6H_5CH_3 + CH_2{=}CHCH_2^- \xrightarrow{k_3} C_6H_5CH_2^- + CH_2{=}CHCH_3 \quad (3)$$

These observations suggest the possibility of catalysis of an ion–molecule reaction.[4] In this communication we report the rate constants for reactions 1, 2, and 3 and the direct observation of a homogeneously catalyzed, gas-phase, ion–molecule reaction: the transfer of a proton from toluene to the allyl anion catalyzed by methanol.

The technique utilized in this study was the trapped ion, pulsed icr method[5] which allows us to observe conveniently reactions as slow as 3. Ion intensities followed as a function of time allowed calculation of rate constants.[6] Exclusive detection of a particular reaction channel was facilitated by application of one-, two-, or three-ion ejection irradiating frequencies. Primary negative ions (OH^-, H^-) from water were used to form the ions during the grid pulse.[5] Hydroxide ion was then ejected from the cell and the process of interest followed.

Because each of the reactions 1–3 is exothermic, the disappearance of allyl anion would be accelerated at high methanol concentration regardless of the size of k_1. However, true catalysis implies an increased rate of formation of benzyl anion and thus requires $k_2 > k_3$. Furthermore, for the effect to be observed at modest methanol concentrations, we require $k_1 > k_3$. In the present case these criteria for catalysis are met, the rate constants[7] being $k_1 = 2.5 \pm 0.3 \times 10^{-10}$, $k_2 = 2.0 \pm 0.2 \times 10^{-10}$, and $k_3 = 7.5 \pm 0.7 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}. In accord with these individually determined rate constants, allyl anion and toluene are converted to benzyl anion and propylene more rapidly in the presence of methanol (see Figure 1). This is true even when the total concentration of reactive neutral gases remains constant. Consistent with our previous observation that toluene lies between ethanol and methanol in acidity,[3] ethanol was found not to catalyze reaction 3. We have also determined the rate constant for the reaction of methoxide ion with ethanol and find $k = 1.2 \pm 0.3 \times 10^{-9}$ cm^3 molecule^{-1} sec^{-1}. This rate constant is significantly larger than any of the others observed above and is typical for ion–molecule reactions which have no apparent activation barrier.

Utilizing our rate constants, we can predict the behavior of the toluene–propylene system with and without methanol and compare experimental and calculated results. In Figure 1, with allyl anion as the sole initial reactant (multiple radiofrequency ejection of all other anions), we see the calculated and observed catalytic effect. Similar agreement between experimental results and calculations was observed for mixtures in which the methanol concentration ranged from 10 to 75% of the toluene concentration. In every case, intermediate buildup of methoxide, followed by its decay and the ultimate appearance of benzyl anion, was observed. Both rates of decay of allyl anion and appearance of benzyl anion were increased when methanol was present.

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[1] (a) For example, see J. E. Parker and R. S. Lehrle, *Int. J. Mass. Spectrom. Ion Phys.*, 7, 421 (1971); L. Friedman, *Advan. Chem. Ser.*, **58**, 87 (1966); A. G. Harrison, J. J. Myher, and J. C. J. Thynne, *ibid.*, **58**, 150 (1966). (b) For other slow ion-molecule reactions, some of which may be governed by spin or other "selection rules," see E. E. Ferguson, *Advan. Electron. Electron Phys.*, 24, 1 (1968); T. F. George and J. Ross, *J. Chem. Phys.*, **55**, 3851 (1971); J. Schaeffer and J. M. S. Henis, *ibid.*, **49**, 5377 (1968); D. K. Bohme and L. B. Young, *J. Amer. Chem. Soc.*, **92**, 7354 (1970).

[2] L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).

[3] (a) L. K. Blair, Ph.D. Dissertation, Stanford University, 1970, and manuscript in preparation; also ref 13a. (b) However, see D. K. Bohme, E. Lee-Ruff, and L. B. Young, *J. Amer. Chem. Soc.*, **94**, 5153 (1972).

[4] For definitions of catalysis see G.-M. Schwab, H. S. Taylor, and R. Spence, "Catalysis," Van Nostrand, New York, N. Y., 1937, p 20; A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, Chapter 9; K. F. Herzfeld, *Z. Phys. Chem.*, **98**, 169 (1921).

[5] R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass. Spectrom. Ion Phys.*, 7, 471 (1971).

[6] An MKS Baratron was used to measure the pressure of gaseous mixtures.

[7] Rate constants can be transformed to M^{-1} sec^{-1} by multiplication by 6.02×10^{20} M^{-1} molecule cm^{-3}.