composition of $C_6H_8D_3O^+$ formed from CD_3COCl gives $C_2D_3O^+$, not $C_2H_3O^+$.

(18) Measurements were made with instrumentation described previously,[1,9,10] 7.8 kV ion accelerating potential. The ion source was modified for higher pressure (~10^{-2} Torr) operation,[1] with pressure (reagent)/pressure (butyl bromide) = 50–100.

(19) Ca. 10% of an isomer other than III or IV is possible; CA spectra of the products of ions from I reacting with furan (reaction 1) and with CH_3COOH are also nearly identical with the spectra from III.

(20) Since completion of this work, an improved computer data acquisition system has been installed. Remeasurement of the CA spectra of I–IV (*without* derivatization) with ±1% precision gave data consistent with these conclusions: a computer error minimization program finds the II spectrum (13 peaks) corresponds to 75% (±20%) III and 25% IV.

(21) E. W. Bittner, E. M. Arnett, and M. Saunders, *J. Am. Chem. Soc.*, **98**, 3734 (1976).

(22) Postdoctoral Fellow, 1974–1975.

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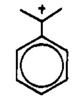
Benzyl Cation. A Long-Lived Species in the Gas Phase?

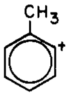
Sir:

Considerable attention has been focused in recent years on providing evidence for or against the stable existence of the benzyl cation (I) in the gas phase. Most recent are investigations by McLafferty and Winkler[1] and by Dunbar and coworkers.[2] The former authors have measured the collisional activation mass spectra of a large number of compounds leading to ions of formula $C_7H_7^+$ and have concluded that in addition to tropylium (II), presumably the lowest energy form, a number of other isomers exist for at least 10^{-5} s. These include the benzyl cation as well as a number of other species (III–VI) of lesser stability. In one series of experiments Shen, Dunbar, and Olah[2a] investigated the distribution of isotopically related product ions in the reaction $C_7H_7^+$, generated in an ion cyclotron resonance spectrometer by electron impact of toluene, with labeled toluene.

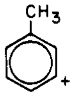


I

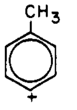
II



III



IV

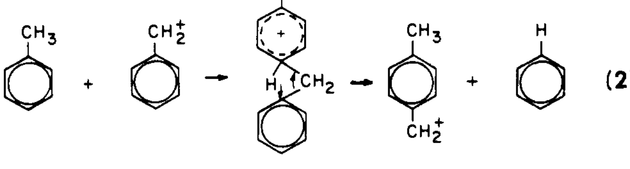


V

VI

$$C_7H_7^+ + C_6H_5CH_3 \longrightarrow C_8H_9^+ + C_6H_6 \qquad (1)$$

From their results with $C_6H_5CD_3$ and $C_6D_5CH_3$, these authors concluded "that of the nine hydrogens in the $C_8H_9^+$ product, three come from the methyl group of neutral toluene, four come from the ring of neutral toluene, and two are drawn in a scrambled fashion from the $C_7H_7^+$ reactant, with some preference to the hydrogens originally on the methyl group". The fact that only two of the product ion's hydrogens originate from $C_7H_7^+$ and that scrambling, although extensive, is incomplete, led Shen, Dunbar, and Olah to propose the following mechanism involving a benzyl cation (eq 2). Shortly thereafter, Dunbar[2b] demonstrated that $C_7H_7^+$, formed in an ICR spectrometer by photodissociation of toluene parent ion, quickly resolves itself into two populations of markedly different reactivity. He assigned the less reactive to tropylium, the more to the benzyl cation.

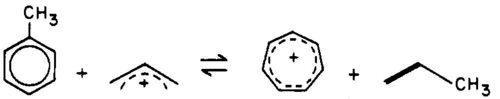


(2)

It appears, therefore, that while there exists substantial evidence in favor of the benzyl cation as a long-lived entity in the gas phase, little is known from experiment about the details of its structure or about its thermochemical stability relative to that of tropylium. It is to these questions that we address ourselves in the present communication. Using pulsed ion cyclotron resonance (ICR) spectroscopy[3] we have established at long times (≤2 s) chemical equilibrium involving transfer of the halide anion between benzyl and *tert*-butyl chloride. The measured free energy for eq 3 at 303 K ($\Delta G° = 0.18 \pm 0.10$ kcal/mol)[4] is in accord with Beauchamp's observation[5] that bromide anion transfer from benzyl to *tert*-butyl bromide is thermoneutral or slightly exothermic. Assuming $\Delta H_f°(298)$ for the *tert*-butyl cation to be 169 kcal/mol,[6,10] we arrive at a value of 217.2 kcal/mol for the heat of formation of $C_7H_7^+$ derived from benzyl chloride.[11] This is higher than previously reported heats for either the benzyl cation (213 kcal/mol[12]) or for tropylium (209 or 212 kcal/mol).[13,14]

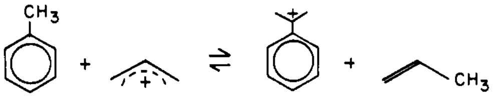
$$C_6H_5CH_2Cl + (CH_3)_3C^+ \rightleftharpoons C_7H_7^+ + (CH_3)_3CCl \qquad (3)$$

In order to clarify the situation with regard to the relative stabilities of the benzyl and tropylium cations, we have determined theoretically their heats of formation by way of ab initio molecular orbital calculations at the split valence shell, 4-31 G level.[15] In particular we have calculated the energetics of the hydride transfer reactions in eq 4 and 5, involving comparison of the benzyl and tropylium cations, respectively, to the allyl cation, a species of similar electronic structure.



ΔE(4-31G) = −16.0 kcal/mole

(4)



ΔE(4-31G) = −25.2 kcal/mole

(5)

Combining these results with the experimental $\Delta H_f°(298)$ for the allyl cation (226 kcal/mol),[12,20] we arrive at theoretical estimates of 217.1 and 207.9 kcal/mol for the heats of formation of benzyl and tropylium, respectively.[21] The first, involving benzyl cation, is in good accord with the experimental heat calculated for the ion resulting from halide abstraction from benzyl chloride; the second is not. Although our theoretical estimate of the heat of formation of the benzyl cation is some 4 kcal/mol higher than the value obtained by Lossing,[12,22] that corresponding to tropylium is in reasonable agreement with the lower of the two experimental determinations.[13]

To further substantiate that it is the benzyl rather than tropylium cation which is actually being observed in the ICR spectrometer, we have measured the free energy of eq 2 at a second (elevated) temperature. Recalling the definition of the free energy

$$\Delta G° = \Delta H° - T\Delta S°$$

it follows that

$$\Delta S° = (\Delta G°_{T_1} - \Delta G°_{T_2})/(T_2 - T_1) \qquad (T_2 > T_1)$$

Assuming that $\Delta S°$ is itself largely temperature independent, we can see that obtaining $\Delta G°$ at two different temperatures gives us the entropy change. To a first approximation $\Delta S°$ may be ascribed exclusively to changes in rotational entropy in going from reactants to products. For a reaction leading to the formation of benzyl cation, $\Delta S°$ is nearly zero within the framework of the model.[23]

$$\Delta S° \approx \Delta S°_{\mathrm{ROT}} = R \ln \left\{ \left[\frac{(I_x I_y I_z)_{\mathrm{benzyl}^+} (I_x I_y I_z)_{t\text{-BuCl}}}{(I_x I_y I_z)_{\mathrm{benzyl\text{-}Cl}} (I_x I_y I_z)_{t\text{-Bu}^+}} \right]^{1/2} \times \left[\frac{\sigma_{\mathrm{benzyl\text{-}Cl}} \sigma_{t\text{-Bu}^+}}{\sigma_{\mathrm{benzyl}^+} \sigma_{t\text{-BuCl}}} \right] \right\} = R \ln \left(0.9 \times \frac{2 \times 81}{2 \times 81} \right) = -0.2 \text{ eu}$$

For the process leading to tropylium, however, the entropy change is sizable.

$$\Delta S° \approx \Delta S°_{\mathrm{ROT}} = R \ln \left\{ \left[\frac{(I_x I_y I_z)_{\mathrm{tropylium}^+} (I_x I_y I_z)_{t\text{-BuCl}}}{(I_x I_y I_z)_{\mathrm{benzyl\text{-}Cl}} (I_x I_y I_z)_{t\text{-Bu}^+}} \right]^{1/2} \times \left[\frac{\sigma_{\mathrm{benzyl\text{-}Cl}} \sigma_{t\text{-Bu}^+}}{\sigma_{\mathrm{tropylium}} \sigma_{t\text{-BuCl}}} \right] \right\} = R \ln \left(0.9 \times \frac{2 \times 81}{14 \times 81} \right) = -4.1 \text{ eu}$$

The temperature of the ICR cell may be varied from 303 to 408 K. Thus, while the free energy for reaction 3 leading to benzyl cation would be nearly independent of temperature over this range, the change in $\Delta G°$ for the corresponding process resulting in tropylium would be 0.43 kcal/mol. The energy changes associated with the formation of the benzyl and tropylium cations are different enough so as to be readily distinguishable at the level of precision with which the equilibrium constant measurements are performed. Experimentally, ΔG for eq 2 at 408 K is 0.23 ± 0.10 kcal/mol. Thus, our measured value for the free energy change over the stated temperature range, $\Delta\Delta G° = 0.05 \pm 0.15$ kcal/mol, is, within experimental error, in accord with the estimate based on rotational entropy changes alone for reaction leading to the generation of benzyl cation.[25] It is not readily interpretable in terms of the process forming tropylium.

In conclusion, both $\Delta H°$ (0.03 ± 0.24 kcal/mol) and $\Delta S°$ (-0.5 ± 1.5 eu), measured by ICR spectroscopy for the halide transfer equilibrium between benzyl and *tert*-butyl chlorides, are consistent with the notion that the $C_7H_7^+$ cation formed is the benzylic system and not the thermodynamically favored tropylium ion.[26] We feel that our results, taken together with those recently obtained by McLafferty and Dunbar and their respective co-workers, provide strong evidence for the stable existence of the benzyl cation in the gas phase.

References and Notes

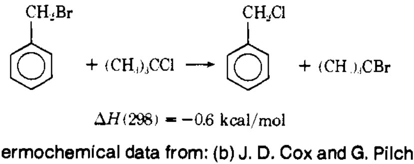
(1) F. W. McLafferty and J. Winkler, *J. Am. Chem. Soc.*, **96**, 5182 (1974).

(2) (a) J. Shen, R. C. Dunbar, and G. A. Olah, *J. Am. Chem. Soc.*, **96**, 6227 (1974); (b) R. C. Dunbar, *ibid.*, **97**, 1382 (1975).

(3) Trapped ion cyclotron resonance spectroscopy: method (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Acc. Chem. Res.*, **4**, 114 (1971); (c) R. T. McIver, Jr. and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971). Representative applications (a) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **93**, 4314 (1971); (b) R. T. McIver, Jr. and J. R. Eyler, *ibid.*, **93**, 6334 (1971); (c) R. T. McIver, Jr. and J. H. Silvers, *ibid.*, **95**, 8462 (1973); (d) R. T. McIver, Jr. and J. S. Miller, *ibid.*, **96**, 4323 (1974); (e) W. J. Hehre, R. T. McIver, Jr., J. A. Pople, and P. v. R. Schleyer, *ibid.*, **96**, 7162 (1974); (f) J. F. Wolf, P. G. Harch, R. W. Taft, and W. J. Hehre, *ibid.*, **97**, 2902 (1975).

(4) Error quoted corresponds to 3 standard deviations.

(5) (a) R. D. Weiting, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 7552 (1974). The heat of the reaction below gives us the difference in energies between the bromide and chloride transfer reactions. Experimental thermochemical data from: (b) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.



$\Delta H(298) = -0.6$ kcal/mol

(6) Such a value has been arrived at by combining the ionization potential of the *tert*-butyl free radical, as determined by Lossing and Semeluk,[7] with its heat of formation recently reported by Tsang.[8] It is in excellent agreement with a value of 169.2 kcal/mol, recently determined by pulsed ion cyclotron resonance spectroscopy.[9]

(7) F. P. Lossing and G. P. Semeluck, *Can. J. Chem.*, **48**, 955 (1970).

(8) W. Tsang, *J. Phys. Chem.*, **76**, 143 (1972).

(9) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, submitted for publication.

(10) Heats of formation for the neutral molecules taken from ref 5b. Because of the uncertainty in the experimental $\Delta H_f°(298)$ for benzyl chloride, our value for the heat of formation of $C_7H_7^+$ could be in error by as much as 2 kcal/mol.

(11) We have actually used the experimental $\Delta H°$ for reaction 2 in the calculation of the heat of formation of $C_7H_7^+$. See subsequent discussion.

(12) F. P. Lossing, *Can. J. Chem.*, **49**, 357 (1971).

(13) G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *J. Am. Chem. Soc.*, **91**, 2823 (1969).

(14) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

(15) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1972); all calculations were carried out using the Gaussian 70 series of computer programs.[16] Standard model geometries[17] have been used for neutral molecules. Structures for the benzyl[3f] and allyl[18] cations have been optimized using the minimal basis set STO-3G method.[19]

(16) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.

(17) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4353 (1967).

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(19) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(20) F. P. Lossing, *Can. J. Chem.*, **50**, 3973 (1972).

(21) Previous experience indicates that energetic comparisons such as those dealt with here (i.e., between species of markedly similar electronic structure) are generally well described using even simple levels of ab initio molecular orbital theory (cf. ref 3e and 3f). Although the absolute heats of formation reported may be somewhat in error (due to the uncertainty in $\Delta H_f°$ for the allyl cation) we strongly suspect that the calculated difference in energies between the benzyl and tropylium cations (9.2 kcal/mol) is correct to within 2 or 8 kcal/mol. Our theoretical results, although seemingly internally consistent, are, therefore, not in good accord with Lossing's estimate for this quantity[12] (1 or 4 kcal/mol) or for that arrived at by Dunbar[2b] (3 kcal/mol).

(22) Lossing[12] has already raised the possibility that, because of rearrangement to tropylium, the heat of formation he reports for the benzyl cation is in fact too low. The theoretical results presented here, in particular with regard to the *difference* in stabilities of the benzyl and tropylium cations, lends support to such a notion.

(23) For discussions, see: (a) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968, p 37; (b) J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley-Interscience, New York, N.Y., 1975, p 1; (c) N. Davidson, "Statistical Mechanics", McGraw-Hill, New York, N.Y., 1962, p 125.

(24) This reference deleted in proof.

(25) Consult ref 9 for comparisons of $\Delta S°$ measured experimentally and calculated on the basis of symmetry number entropy changes alone for simple ion–molecule reactions involving species of known geometrical structure. In all cases agreement is within 10–20%.

(26) Although our measured value of $\Delta\Delta G°$ does not rule out the possibility of $C_7H_7^+$ having a geometrical structure such as V, unpublished ab initio calculations by Dill, Schleyer, and Pople[27] show that such a species is very unstable relative to benzyl and tropylium cations and would result in an energy of eq 3 far different from the experimental value.

(27) J. A. Pople, private communication.

(28) Alfred P. Sloan Fellow, 1974–1976.

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Novel Carbon–Hydrogen Bond Cleavage by Bis(dimethylphosphino)ethane Complexes of Iron, Ruthenium, and Osmium

Sir:

We wish to report the first transition metal complex capable of rapidly cleaving a variety of C–H bonds (activated sp^3, aromatic sp^2, and sp) under mild conditions, resulting in adducts which can be fully characterized. The new complex $Fe(dmpe)_2H(C_{10}H_7)$ (**1**) ($C_{10}H_7$ = 2-naphthyl, dmpe = $Me_2PCH_2CH_2PMe_2$) prepared by the reaction of Fe-