An Estimate of the Stabilization Energy of the Benzyl Radical *via* HF$^+$ Infrared Chemiluminescence from $C_6H_5CH_3 + F \rightarrow HF^+ + C_6H_5CH_2\cdot$

Sir:

Hydrogen fluoride infrared chemiluminescence from the reactions $RCH_3 + F \rightarrow RCH_2 + HF^+$ (v, J), where RCH_3 = toluene and mesitylene-d_3, has been observed and interpreted. The highest observed HF$^+$ (v, J) states lie 11.2 kcal mol^{-1} below the limit imposed by the accepted thermochemical equilibrium value of $D_0(C_6H_5$-CH_2-H).[1] In addition the fraction of available energy appearing in HF$^+$ vibration is significantly below that found for other RCH_3 molecules. This is a strong indication that much of the resonance energy of the benzyl and mesityl radicals is not available to the initially formed HF$^+$ but is released later on the reaction coordinate. Thus the thermodynamically equilibrated benzyl and mesityl radicals are stabilized by at least 11.2 kcal mol^{-1} relative to the energy configurations which are initially formed by the H atom transfer (abstraction) process.

Previous investigations of HF$^+$ infrared chemiluminescence with other polyatomic hydride molecules[2,3] have established that the highest observed vibration–rotation states of HF$^+$ are in good agreement with known bond dissociation energies for those cases where the radical is not significantly stabilized.[2,3] For the benzyl radical, the total stabilization energy should be essentially equal to the resonance energy and results from rehybridization of the methylene carbon to an sp^2 configuration with delocalization of the odd p electron.

The experiments were performed in a cold-walled vessel at 10^{-4} Torr, conditions which have been shown to arrest vibrational relaxation but only partially arrest rotational relaxation.[2-4] The vibrational and rotational population analyses were obtained by matching experimental spectra to spectra which were simulated by computer using known transition probabilities.[2,3]

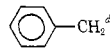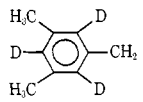In order to calculate the energy available to the HF$^+$ product, E_{tot}, we have used eq 1

$$E_{tot} = -\Delta H_0^\circ + E_a + 3RT \tag{1}$$

where ΔH_0° is the exothermicity of the reaction at 0°K and E_a is the Arrhenius activation energy.[5] The quantity, $E_a + 3RT$, is the mean energy of reactive collisions calculated from Tolman's definition of E_a[6] and the assumption that only translational and rotational energy are effective in promoting reaction. We used $E_a = 1.0$ kcal mol^{-1} based upon a subjective appraisal of published data for F + RH reactions.[7] Previous

results with molecules which do not give resonance stabilized radicals indicate that the error in the calculation of E_{tot} is ca. 1-2 kcal mol^{-1}.[2a,5,8]
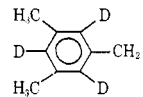
In Table I we report the observed and calculated

Table I. Observed and Calculated Energies for F + RH Reactions

R	Calcd^a E_{tot}, kcal mol^{-1}	Obsd E_{tot}, kcal mol^{-1}	$E_{stab}(R\cdot)$, kcal mol^{-1}
⟨benzyl⟩—CH_2^{d}	54.6 ($v = 5$, $J = 7$)^b	43.4 ($v = 4$, $J = 4$)	≥ 11.2
⟨mesitylene-d_3⟩—CH_2 ^{e}	54.6^c ($v = 5$, $J = 7$)^b	43.4 ($v = 4$, $J = 4$)	$\geq 11.2^c$

^{a} Method of calculation given in text. ^{b} The highest allowed HF$^+$ v and J states are shown in parentheses. ^{c} E_{tot} is assumed to be the same as for benzyl. ^{d} Six experiments all showed $v = 4$ and $J = 4$ as the highest state. ^{e} Two experiments with mesitylene and two experiments with mesitylene-d_3 all showed $v = 4$ and $J = 4$ as the highest state.

values of E_{tot} for the reactions of toluene and mesitylene-d_3. The highest observed v and J states are the same for both reactions and lie 11.2 kcal mol^{-1} below the v and J states which are expected on the basis of the calculated E_{tot}. A further indication of a large stabilization energy for benzyl comes from the vibrational energy partitioning data reported in Table II.

Table II. Observed Vibrational Energy Partitioning for F + RH Reactions

R	Normalized populations^a				%E_v^{f}
	$v = 1$	$v = 2$	$v = 3$	$v = 4$	
⟨mesitylene-d_3⟩—CH_2 ^{b}	0.19	0.37	0.4	0.04	46
$C_6H_5CH_2$^{c}	0.25	0.39	0.29	0.03	e
C_6H_5^{d}	0.70	0.30			56

^{a} The relative standard error for the population of each level is 5% or less. ^{b} Mean of two HF$^+$ fundamental scans. ^{c} Mean of five HF$^+$ fundamental scans. ^{d} Mean of three HF$^+$ fundamental scans. ^{e} For toluene %E_v is not well defined since two types of C–H bonds contribute to the HF$^+$ product. The enhancement of the $v = 1$ and 2 populations for toluene relative to mesitylene-d_3 is expected since reaction at the ring position gives HF($v \leq 2$). ^{f} %E_v is calculated assuming zero population for HF ($v = 0$) (see ref 4); %$E_v = \Sigma_{v=1}^4 n_v E_v / E_{tot}$, with E_{tot} being the calculated value.

Mesitylene-d_3 was used to obtain energy partitioning data free of the contribution to HF$^+$ product arising from the aromatic C–H bonds. Preparation of the large amount of mesitylene-d_3 (ca. 30 ml) needed for reliable results was accomplished in $D_2O + D_2SO_4$ mixtures at 70°. Greater HF$^+$ emission intensity was observed with mesitylene than with toluene, probably

(1) R. Walsh, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 650 (1966).

(2) (a) H. W. Chang and D. W. Setser, *J. Chem. Phys.*, **58**, 2298 (1973); (b) W. H. Duewer and D. W. Setser, *ibid.*, **58**, 2310 (1973).

(3) K. C. Kim and D. W. Setser, *J. Phys. Chem.*, **77**, 2493 (1973).

(4) J. C. Polanyi and K. B. Woodall, *J. Chem. Phys.*, **57**, 1574 (1972).

(5) ΔH_0° was calculated from ΔH°_{298}, the normal mode frequencies of toluene given by Scott, *et al.*, *J. Phys. Chem.*, **66**, 911 (1962), and assumed frequencies for benzyl. The value of ΔH°_{298} was obtained from Benson's thermodynamic equilibrium value of $D(C_6H_5CH_2-H)$ (ref 1) and Chupka and Berkowitz's value of $D(H-F)$: W. A. Chupka and J. Berkowitz, *J. Chem. Phys.*, **54**, 5126 (1971).

(6) (a) R. C. Tolman, *J. Amer. Chem. Soc.*, **42**, 2506 (1920); (b) M. Menzinger and R. Wolfgang, *Angew. Chem., Int. Ed. Engl.*, **8**, 438 (1969).

(7) (a) K. H. Homann, W. C. Soloman, J. Warnatz, H. Gg. Wagner, and C. Zetsch, *Ber. Bunsenges. Phys. Chem.*, **74**, 585 (1970); (b) J. Warnatz, H. Gg. Wagner, and C. Zetsch, *Ber. Bunsenges. Phys. Chem.*, **75**, 119 (1971); (c) R. Foon and G. P. Reid, *Trans. Faraday Soc.*, **67**, 3513

(1971); (d) R. Foon and N. A. McAskill, *ibid.*, **65**, 3005 (1969). (e) R. F. Walker and M. A. A. Clyne (private communication).

(8) The experimental determination of E_{tot} is dependent upon the spacing of J states in the vicinity of the highest observed J. Hence the uncertainties in E_{tot} and the estimated $E_{stab}(C_6H_5CH_2)$ increase with increasing J. The finite width of the reactive collision energy distribution and uncertainties in heats of formation also contribute to error.

because the nine methyl hydrogens result in a greater cross-section for the desired reaction.

It has been established[2,3] that reactions of F with primary C–H bonds are characterized by $\%E_v = 60 \pm 5$. For the reaction F + mesitylene-d_3 we find $\%E_v = 47$; this lowered fraction of energy released to HF$^+$ is a very sensitive indicator of the presence of radical stabilization since it describes the shape of the detailed vibrational energy distribution of the HF$^+$ product.

The constancy of $\%E_v$ for other R–CH$_3$ reactions[2,3] indicates that the entrance valleys of the surfaces for this class of reaction are nearly invariant and suggests that the relaxation of benzyl occurs on a slower time scale (hence later on the reaction coordinate) than the H atom transfer. The methylene torsion is expected to be the slowest component in the reorganization of benzyl and this serves to establish the relaxation time at *ca.* 10^{-13} sec. Three-body (R–H + F) trajectory calculations on a LEPS type potential energy surface indicate that the time scale for direct H atom abstraction by F is less than 10^{-14} sec.[9,10]

An unfortunate complication is that some reactive collisions are expected to occur by indirect encounters,[9,11] either complex encounters where the separation of HF$^+$ from R is not simple or encounters where the initially formed HF$^+$ undergoes a second collision with R.[9] In such encounters some of the stabilization energy of the R fragment may be transferred to HF$^+$. Because of this problem and the possibility that H atom transfer and the relaxation of the radical fragment may not be completely separated, even for simple collisions, we infer that our experimental measurement of E_{stab}. (C$_6$H$_5$CH$_2$) must represent a lower limit.[12]

Although these problems detract from the quantitative interpretation of our data, the present experiments represent the first direct[12] dynamical evidence concerning the disposal of the resonance stabilization energy of the radical fragment produced by an H atom abstraction reaction and, consequently, of the time scale for release of this energy. The method provides a straightforward and sensitive test for the presence of stabilization energy in polyatomic radicals.

(9) R. L. Johnson, K. C. Kim, and D. W. Setser, *J. Phys. Chem.*, 77, 2499 (1973).

(10) The time scale for the atom transfer process is strongly dependent upon the mass of the central atom as well as other dynamical features. In general the fastest process is transfer of an H atom (the lightest possible mass) with a low threshold energy. Thus RH + F reactions are ideal probes for radical stabilization energy, E_{stab}(R).

(11) For a discussion see J. C. Polanyi, *Accounts Chem. Res.*, 5, 161 (1972).

(12) Benson, *et al.* (ref 1), have found D_{298}(C$_6$H$_5$CH$_2$–H) = 85 kcal mol^{-1} which is anomalously low for a primary C–H bond. They have obtained the estimate, E_{stab}(C$_6$H$_5$CH$_2$) = 13 $\pm$ 1 kcal mol^{-1}, based upon comparison of the above value with D_{298}(CH$_3$CH$_2$–H) = 98 kcal mol^{-1}. Our lower limit of 11.2 kcal mol^{-1} is in good agreement with the above estimate. The well-known low reactivity of benzyl (and other resonance stabilized radicals) provides further indirect evidence. For discussion, see M. Szwarc, *Chem Rev.*, 47, 75 (1950), and references therein.

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Relative Iron–Carbon and Iron–Silicon Bond Strengths in Derivatives of (η-Cyclopentadienyl)dicarbonyliron

Sir:

The transition metal–silicon σ-bond[1] has generally been considered to be substantially stronger than the corresponding metal–carbon σ-bond, presumably due to metal–silicon d$_\pi$–d$_\pi$ bonding.[2] This hypothesis appears to be supported by the known bond dissociation energies for transition metal–silicon and –carbon σ-bonds, which indicate the former to be stronger by 60–80 kcal,[3–5] and the instability of many alkyl complexes which have well-behaved organosilyl analogs. Recently, however, it has been proposed that the instability of many alkyl complexes is not a consequence of an inherently low metal–carbon bond strength but is rather due to the availability of a number of low energy degradative pathways.[6] Notable among these pathways is alkene formation *via* elimination of the transition metal and a β-hydrogen as the metal hydride. Since derivatives of silaethylene are apparently extremely reactive and or unstable, it has been proposed that part of the thermal stability of organosilyl complexes must be attributed to the reluctance of these complexes to decompose by elimination of the metal hydride.[7] We now wish to present chemical evidence which demonstrates that, in the case of derivatives of (η-cyclopentadienyl)dicarbonyliron, the iron–carbon and the iron–silicon σ-bond strengths are not significantly different and the possibility that the iron–carbon is stronger must be considered.

Our interest in the transition metal chemistry of strained and reactive olefins led us to prepare complexes **1**, **2**, and **3** with a view toward transforming these substances into cationic silaisobutylene complexes. The silyl complexes (**1–3**) were prepared by distilling an equimolar quantity of chlorosilane, ClCH$_2$Si(CH$_3$)$_{3-n}$Cl$_n$ (n = 1, 2, or 3), under vacuum onto a 0.4 M solution of sodium (η-cyclopentadienyl)dicarbonylferrate in tetrahydrofuran at $-196°$, warming the reaction mixture to room temperature, and stirring magnetically for 30 min. Complexes **1** and **2** were isolated by vacuum distilling the solvent at 0°, extracting the residue with *n*-hexane, and recrystallizing from *n*-hexane at $-78°$. Vacuum (10^{-5} mm) sublimation of the residue gave **3**. The yields were about 60% in all cases.[8]

(1) Silyl and silylmethyl complexes have been recently reviewed; C. S. Cundy, B. M. Kingston, and M. F. Lappert, *Advan. Organometal. Chem.*, 11, 253 (1973).

(2) (a) R. B. King, K. H. Pannell, C. R. Bennett, and M. Ishaq, *J. Organometal. Chem.*, 19, 327 (1969); (b) A. G. Robiette, G. M. Sheldrick, R. N. F. Simpson, B. J. Aylett, and J. M. Campbell, *ibid.*, 14, 279 (1968).

(3) The bond dissociation energies for Cl$_3$Si–, F$_2$MeSi–, and F$_3$SiCo(CO)$_4$ have been reported as 126 $\pm$ 25, 127 $\pm$ 15, and 105 $\pm$ 12 kcal. The bond energies are dependent on the value used for $\Delta H_f°$ of Co$_2$(CO)$_8$ and may therefore be approximately 30 kcal lower. F. E. Saalfield, M. V. McDowell, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, 92, 2324 (1970).

(4) Very few transition metal–carbon σ-bond dissociation energies have been determined and these are listed below: Me–Pt (CpPtMe$_3$), 39 $\pm$ 5;[5a] Et–Ti (Cp$_2$TiClEt), 36 kcal.[5b]

(5) (a) K. W. Egger, *J. Organometal. Chem.*, 24, 501 (1970); (b) E. A. Fushman, E. D. Potyagalio, and N. M. Chirkov, *Izv. Akad. Nauk SSSR, Ser. Kim.*, 715 (1971).

(6) G. Wilkinson, *Pure Appl. Chem.*, 30, 627 (1972).

(7) A. G. MacDiarmid, Y. L. Baay, J. F. Bald, A. D. Berry, S. K. Gondal, A. P. Hagen, M. A. Nasta, F. E. Saalfield, and M. V. MacDowell, *Pure Appl. Chem.*, 19, 431 (1969).

(8) Satisfactory carbon, hydrogen, and/or halogen analyses have been obtained for all new compounds.