Both III and IV exhibit only a sharp doublet for the methoxy protons, and for IV this requires that the phosphite ligands adopt the unambiguous pseudocis configuration indicated, with essentially zero P–P coupling. This also provides the basis for the simplifying assumptions in the interpretation of the spectrum of VI, discussed above.

In the spectrum for V, Figure 1, we see a virtual triplet whose central band is of lower relative intensity than that of VI and whose maximum is displaced somewhat to lower field (τ 6.22) from the midpoint (τ 6.23) of the two outer peaks. This is the result of near coincidence in what we assign as a doublet for the phosphite (L′) trans to CO and a virtual triplet of the two phosphites trans to each other (L and L′′). The near superposition of an outer 1:1 doublet and a virtual 1:2:1 triplet requires that the apparent triplet have peaks of relative intensity 1:1.33:1, close to that observed.

The most prominent feature to be noted in the nmr spectra of III–VI is the single chemical shift for metal–hydrogen in all the derivatives. Each hydrogen appears also to be equivalently spin coupled to all the phosphorus nuclei in any particular complex. Whatever else may be said about the structures of these substituted clusters, it is clear that some form of intramolecular tautomerism is occurring in which the chemical shift of hydrogen and its coupling to phosphorus becomes averaged. The increase in averaged coupling constant from III through VI is interpretable as due to an increase in average proximity of H to P as ligand substitution is increased.

The observed equivalence of the environment of the hydrogen atoms could come about from their rapid exchange of positions along the edges and in part from an intramolecular rotation of the $Ru(CO)_2L$ groups about the C_3 axes of the tetrahedron. The second of these two possibilities can be eliminated on two grounds. In IV, rotation of the $Ru(CO)_2L$ groups would bring the phosphite ligands into trans positions where P–P coupling would occur, as it does in V and VI, and a time-averaged virtual triplet should result, which is *not* the case. In addition, low-temperature studies of VI in dichlorofluoromethane showed no change in the nmr spectrum on cooling to −100°. This suggests a very low activation energy for the tautomeric process, consonant with exchange of hydrogen atoms,[9] parallel to hydrogen exchange in boron hydrides.[10]

We believe similar degenerate tautomerism very likely is occurring in the unsubstituted carbonyl hydride II and could be ascertained from the ^{13}C satellites of the metal hydrogen resonance; solubility problems, however, have thus far prevented us from observing these. Hydrogen tautomerism in the edge-bridged H_4Ru_4 group might well involve face bridging in the transition state. It is interesting to note in this connection that the face-bridged hydrogen atoms of I are easily converted[2] to what is most certainly edge bridging in tetrahedral $[H_6Re_4(CO)_{12}]^{2-}$. Tautomerism in I is therefore also possible, as it is in any cluster with unoccupied polyhedral sites lying energetically close to the sites occupied by the bridging hydrogen in the ground-state structure.

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(9) Time-averaged equivalence of ligands has been observed in $C_4H_6Fe(CO)(PF_3)_2$ and $C_4H_6Fe(PF_3)_3$ at room temperature, but rotational motion was effectively frozen out at about −100°; see J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970), and references cited therein.

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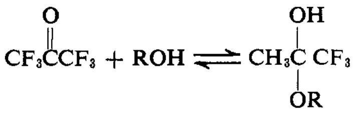
Thermochemistry of Carbonyl Addition Reactions. I. Addition of Water and Methanol to Hexafluoroacetone

Sir:

While the thermochemistry of water and methanol addition to carbonyl compounds has been of significant interest, the studies have been limited to the solution phase[1] and little thermochemical data are available on the formation of carbonyl hydrates or hemiacetals in other phases where solvation and intermolecular interactions play a smaller role. We wish to report the heat of addition of methanol and water to a ketone in the solution, "standard state," and gas phases at 25°.

Hexafluoroacetone (HFA) reacts rapidly and completely with water and methanol to form the stable hydrate[2] **1**, mp 43–45° and hemiacetal[3] **2**, bp 95°,



$$CF_3\overset{\overset{\displaystyle O}{\|}}{C}CF_3 + ROH \rightleftharpoons CH_3\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}CF_3$$

1, R = H
2, R = CH_3

respectively. The heats of addition in solution were determined by adding a known quantity of HFA gas to distilled water or anhydrous methanol in a solution calorimeter described elsewhere.[4] The heats of solution and vaporization of the hydrate and hemiacetal were determined by direct calorimetry and the data were treated according to the enthalpy cycle. Since

$$\begin{tikzcd}
\mathrm{HFA(g)} & +\ \mathrm{ROH(g)} \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{HFA\cdot ROH(g)} & \Delta H_r{}^{\circ}{}_{(g)} \\
\mathrm{HFA(g)} \arrow[d, "\Delta H_{(soln)}"'] & +\ \mathrm{ROH(l)} \arrow[u, "\Delta H_v"'] \arrow[d, "\Delta H_{(soln)}"'] \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{HFA\cdot ROH(l\ or\ c)} \arrow[u, "\Delta H_v"'] \arrow[d, "\Delta H_{(soln)}"'] & \Delta H_r{}^{\circ} \\
\mathrm{HFA(soln)} & +\ \mathrm{ROH(soln)} \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{HFA\cdot ROH(soln)} & \Delta H_r{}^{\circ}{}_{(soln)}
\end{tikzcd}$$

HFA is added to the solvent $\Delta H_{exptl} = \Delta H_{soln}(HFA) + \Delta H_r{}^{\circ}{}_{(soln)}$ so that $\Delta H_r{}^{\circ} = \Delta H_{exptl} + \Delta H_{soln}(ROH) - \Delta H_{soln}(adduct)$ and $\Delta H_r{}^{\circ}{}_{(g)} = \Delta H_r{}^{\circ} + \Delta H_v(adduct) - \Delta H_v(ROH)$. These expressions can be simplified further since dilute solutions are involved (*ca.* 4 × 10^{-3} *M* in adduct), $\Delta H_{soln}(ROH) \cong 0$. The experimental quantities are given in Table I.

The data clearly show that the heat of hydration and hemiacetal formation of HFA are reasonably close in any one phase. The methanol addition is slightly more exothermic in the "standard state" and slightly less in the gas phase. Presumably, the same trend will obtain

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(1) (a) R. P. Bell, *Advan. Phys. Org. Chem.*, **4**, 1 (1966); (b) J. Kurz, *J. Amer. Chem. Soc.*, **89**, 3524 (1969); J. M. Bell, D. G. Kubler, P. Sartwell, and R. G. Zepp, *J. Org. Chem.*, **30**, 4284 (1965).

(2) W. J. Middleton and R. V. Lindsey, *J. Amer. Chem. Soc.*, **86**, 4948 (1964).

(3) I. L. Knunyanto, T.-Y. Chen, and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **686** (1960).

(4) F. E. Rogers, *J. Phys. Chem.*, **75**, 1734 (1971).

Table I. Enthalpies (25°, kcal/mol)

Adduct	ΔH_{exptl}	ΔH_{soln}	ΔH_v	$\Delta H_r°$	$\Delta H_r°_{(g)}$	$\Delta H_r°_{(\text{soln})}$[a]
$(CF_3)_2C(OH)_2$	−24.4 ± 0.2	−3.99 ± 0.04	17.0 ± 0.2	−20.4 ± 0.2	−13.9 ± 0.4	−22.4 ± 1.2
$(CF_3)_2C(OH)OCH_3$	−24.7 ± 0.3	−3.44 ± 0.02	17.4 ± 0.2	−21.3 ± 0.3	−12.8 ± 0.5	−22.7 ± 1.3

[a] Derived from the relation $\Delta H_r° - \Delta H_r°_{(\text{soln})} = \Delta H_{\text{soln}}(\text{HFA}) - \Delta H_{\text{soln}}(\text{adduct})$, assuming $\Delta H_{\text{soln}}(\text{HFA}) = -2 \pm 1$ kcal/mol.

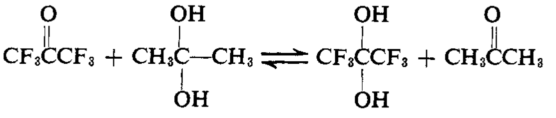
with other carbonyl compounds. In both cases the "standard-state" reaction differs only slightly from the heat of reaction in solution. According to the enthalpy cycle, this latter difference is limited to the difference in the heat of solution of the carbonyl compound and its adduct. The heat of solvation for both reactions, $\Delta H_r°_{(\text{soln})} - \Delta H_r°_{(g)}$, is about −9 kcal/mol. Since it is unlikely that the heat of solvation of the reactants will exceed those of the product, the heat for the solution reaction should represent the maximum or limiting value for this type of reaction. The scarcity of reliable data makes comparison with other gas-phase reactions undesirable; however, comparison can be made with the hydration of similar carbonyl compounds in solution.

Table II shows that the heat of hydration of HFA is much larger than analogous compounds and also the heat of reaction increases with halogen substitution (*ca.* 3–3.5 kcal/halogen atom). Levy, Cargioli, and Racela have reported that multiple halogen substitution also produces an approximately linear decrease in ketone basicity (*ca.* 2 H_0 units per halogen).[5] The heat of hydration of acetone is too low to have been measured reliably but assigning $\Delta H_{r(\text{soln})} = -1 \pm 1$ kcal/mol allows the formulation of the following equilibrium

Table II. Heats of Hydration of Carbonyl Compounds (kcal/mol)

Compd	$\Delta H_r°_{(\text{soln})}$
$CH_3C(=O)CH_2Cl$	−2.0[a]
$CH_3C(=O)CHCl_2$	−5.5[a]
CH_3CHO	−5.1[a]
CCl_3CHO	−14.0[a]
$CF_3C(=O)CF_3$	−22.4

[a] Reference 1a.



$$CF_3C(=O)CF_3 + CH_3C(OH)_2CH_3 \rightleftharpoons CF_3C(OH)_2CF_3 + CH_3C(=O)CH_3$$

$$\Delta H = -21 \text{ kcal/mol}$$

The rather large enthalpy associated with the disproportionation reaction can be analyzed in terms of carbonyl group stabilization. In substituted alkenes it is customary to regard differences in heats of hydrogenation as a measure of the stabilizing effect of the substituent. Similarly the heats of hydrogenation of formaldehyde (−22 kcal/mol) and acetone (−13 kcal/mol)[6] show a 9-kcal stabilizing effect for two methyl groups at a carbon–oxygen double bond. To account for the enthalpy in the equilibrium reaction above, one may then infer that two CF_3 groups destabilize a carbonyl bond by *ca.* 12 kcal. This conclusion is in agreement with the remarkable reactivity of HFA[7] in carbonyl addition reactions.

Another method of assessing strain in a molecule is the comparison of experimental heats of formation with calculated heats of formation by a method of group increments.[8] The heats of formation derived from our experimental data were compared to values calculated from the group increment scheme of Cox and Pilcher.[8b] These values are given in Table III.

Table III. Heats of Formation (25°, kcal/mol)

Compd	State	$\Delta H_f°$ Obsd	$\Delta H_f°$ Calcd	Strain (Obsd − calcd)
$(CF_3)_2C(OH)_2$	(g)	−370.7	−409.13	38.4
	(c)	−387.7		
$(CF_3)_2C(OH)OCH_3$	(g)	−359.9	−405.20	45.3
	(l)	−377.3		
$CF_3C(=O)CF_3$	(g)	−299[a]	−352.8	53.8

[a] Reference 7.

Table III predicts a large amount of strain in HFA which is relieved in the hemiacetal or hydrate by 9 and 15 kcal, respectively. This strain is not apparent in the structure of HFA; the bond angles, carbon–oxygen, and carbon–carbon bond distances of HFA[9] and acetone[10] are the same within the combined experimental errors.

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[5] G. C. Levy, J. D. Cargioli, and W. Racela, *J. Amer. Chem. Soc.*, **92**, 6238 (1970).

[6] Derived from heat of formation data reported in J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970.

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[9] G. Boulet, *Diss. Abstr.*, **25**, 3283 (1964).

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Transition Metal Promoted Isomerizations of Highly Strained Polycyclic Systems. A Mechanistic Insight[1]

Sir:

The rearrangement of highly strained ring systems by transition metal catalysts has recently attracted considerable attention. Although many examples of such rearrangements are now known, relatively little is available in the line of definitive evidence concerning the mechanism of these isomerizations. A typical case is that of tricyclo[4.1.0.0^{2,7}]heptane (I), which,

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[1] Paper XXIV on the Chemistry of Bent Bonds. For the previous paper in this series, see P. G. Gassman, G. R. Meyer, and F. J. Williams, *Chem. Commun.*, in press.