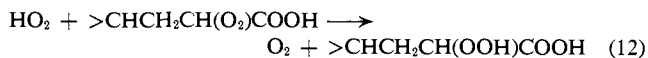
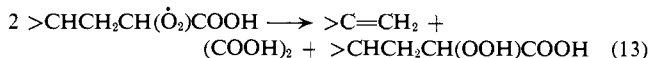


where $>CHCH_2CH_2COOH$ represents the side chain of the glutamic acid residue. Peroxy radicals of the type formed in reaction 11 are relatively long-lived and we suggest they are subsequently removed through the competing reactions



and



Degradation reactions akin to reaction 13 have been described by Russell⁶ and by Durup, *et al.*⁷ It is seen that the product $>C=CH_2$ in the above nomenclature corresponds to the acrylic acid derivative $RCONHC(=CH_2)R$ (a tautomeric form of the dehydropeptide, $RCON=C(CH_3)R$), which on hydrolysis yields ammonia and pyruvic acid. Also, we conclude from the results obtained with N-acetylglutamic α -methyl ester that the relative rates of reactions 12 and 13 are essentially independent of the degree of ionization of the reacting species over the pH range 3 to 8.

Now, to explain the pronounced effect of pH on $G(NH_3)$ and $G(\text{pyruvic})$ from PGA we note first that a unique characteristic of the radiation chemistry of a macromolecular substance in aqueous solution is that each molecule undergoes reaction with a relatively large number of OH radicals even at the lowest practicable dosages. For example, with a 0.15% solution of PGA, a γ -ray dose of 3×10^{18} e.v./g. produces but one OH per 100 glutamic acid residues but at the same time this corresponds to about 20 OH radicals per PGA molecule (mol. wt. 140,000). However, since PGA above pH 6 has the random coil configuration,⁸ the various segments of the macromolecule are free to interact both intermolecularly and intramolecularly, and we find at pH >6 no essential differences between the macromolecule and the low molecular weight model from the standpoint of product yields. But, as the pH of the solution is decreased, PGA undergoes a coil \rightarrow helix transition over the pH range 6 to 4.5 which as we have noted is the significant pH range of Figure 1. With PGA in the helix form, the peroxy radicals are frozen in a fixed spatial arrangement and it is obvious that the probability of reaction 13 is greatly reduced; hence reaction 12 is favored and as a result $G(NH_3)$ and $G(\text{pyruvic})$ decrease as seen in Figure 1.⁹

(6) G. A. Russell, *Chem. Ind. (London)*, 49, 1483 (1956).

(7) M. Durup, J. Durup, F. Kuffer, and M. Magat, *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva*, 29, 143 (1958).

(8) See, for example, J. Applequist and J. L. Breslow, *J. Am. Chem. Soc.*, 85, 2869 (1963).

(9) This work was done under the auspices of the U. S. Atomic Energy Commission.

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Tetrafluoroethylene Complexes of Transition Metals

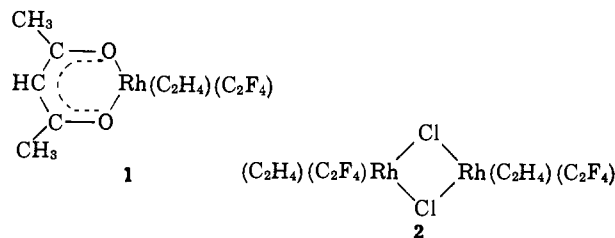
Sir:

Since the first preparation of perfluorotetramethylene-iron tetracarbonyl,¹ there have been numerous attempts

(1) K. F. Watterson and G. Wilkinson, *Chem. Ind. (London)*, 991

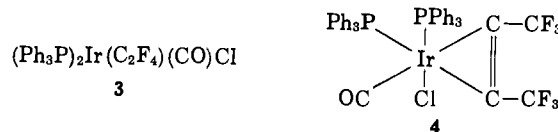
to make transition metal complexes of tetrafluoroethylene (TFE).² We wish to report the isolation of the first simple TFE complexes, compounds of rhodium or iridium, from which the fluoroolefin can be displaced under mild conditions.

The rhodium complexes are obtained by *displacing* ethylene from 2,4-pentanedionatobis(ethylene)rhodium-(I)³ or μ -dichlorotetraethylenedirhodium(I)⁴ with tetrafluoroethylene at room temperature and atmospheric pressure. The products (1 and 2) retain one ethylene ligand per metal atom which is not displaced by continued exposure to TFE. Ethylene but not TFE is



displaced from 1 or 2 by phosphines, amines, nitriles, or cyanide ion. Both ethylene and TFE are displaced by 1,5-cyclooctadiene or carbon monoxide.

The iridium complex 3 is prepared by the *addition* of TFE to chlorocarbonylbis(triphenylphosphine)iridium(I).⁵ It readily evolves TFE on standing in benzene



solution at 25 or at 100° under vacuum. Its hexafluoro-2-butyne analog 4 is even more remarkable in that it evolves butyne reversibly *in the solid state*.

The TFE complexes of rhodium (1 and 2), in contrast to the σ -bonded fluoroolefin complexes obtained earlier,^{1,2,6} show chemical properties similar to those of conventional olefin complexes based on σ -donor- π -acceptor bonds.⁷ The facile displacement of TFE by the chelating diolefin, 1,5-cyclooctadiene, is reminiscent of conventional olefin-exchange reactions. Contrary to this chemical evidence, however, the spectra of the iridium complexes 3 and 4 suggest extensive σ -bonding. Thus, the bonding of hexafluorobutene in 4 may approach that of a $[C_4F_6]^{2-}$ ion coordinated to iridium(III) by two σ -bonds, analogous to that of the oxygen ligand in $(Ph_3P)_2(CO)IrCl(O_2)$.⁸ The infrared spectrum of 4 shows a C=C stretching vibration at 1770 cm^{-1} like that in $(Ph_3P)_2Pt(CF_3CCCF_3)$ ^{8a} and intermediate between the C=C frequencies in⁹ 5 and 6.

Ethylenebis(triphenylphosphine)nickel¹⁰ undergoes ethylene displacement when it is treated with TFE, but

(1959); *ibid.*, 1358 (1960); H. H. Hoehn, G. Wilkinson, *et al.*, *J. Chem. Soc.*, 2738 (1961).

(2) This topic has been reviewed by P. M. Treichel and F. G. A. Stone in "Advances in Organometallic Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1964, p. 143.

(3) R. Cramer, *J. Am. Chem. Soc.*, 86, 217 (1964).

(4) R. Cramer, *Inorg. Chem.*, 1, 722 (1962).

(5) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, 83, 2784 (1961).

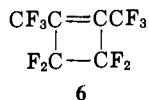
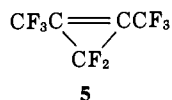
(6) (a) J. L. Boston, S. O. Grim, and G. Wilkinson, *J. Chem. Soc.*, 3468 (1963); (b) M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 365 (1963).

(7) M. J. S. Dewar, *Bull. soc. chim. France*, 18, C79, (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(8) L. Vaska, *Science*, 140, 809 (1963).

(9) W. Mahler, *J. Am. Chem. Soc.*, 84, 4600 (1962).

(10) G. Wilke and G. Hermann, *Angew. Chem.*, 74, 693 (1962).



a gross redistribution of phosphine ligands occurs to give $(\text{Ph}_3\text{P})_3\text{Ni}(\text{C}_2\text{F}_4)$.

Preparation of **1** was effected by bubbling TFE through a suspension of acetylacetonatodiethylenorhodium in ether for 30 min. Cooling to -78° gave yellow crystals of **1**, m.p. $78-79^\circ$. *Anal.* Calcd. for $\text{C}_9\text{H}_{11}\text{F}_4\text{O}_2\text{Rh}$: C, 32.8; H, 3.34; mol. wt., 330. Found: C, 33.3; H, 3.65; mol. wt., 350. The iridium-TFE complex **3** was obtained as off-white crystals by shaking a toluene solution of $(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCl}$ with TFE at 3 atm. for 7 days. *Anal.* Calcd. for $\text{C}_{39}\text{H}_{30}\text{ClF}_4\text{IrOP}_2$: C, 53.2; H, 3.44; F, 8.63. Found: C, 53.6; H, 3.74; F, 8.85. The iridium-hexafluorobutylene complex **4** was obtained by stirring a toluene solution of $(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCl}$ with hexafluorobutylene at 1 atm. for 16 hr. Pyrolysis of 0.85 mmole of **4** at 105° gave 0.84 mmole of pure $(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCl}$, 0.79 mmole of hexafluoro-2-butyne, and a trace of toluene. The infrared spectra of **1** and **3** showed two CF stretching bands at longer wave length than those of TFE. The CO absorption bands of **3** and **4** appeared at 2040 and 2025 cm^{-1} , respectively, vs. 1965 cm^{-1} for $(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCl}$.

Further details of the chemistry and spectral properties of these compounds will be published soon.

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A Large Solvation Enthalpy Effect in Highly Aqueous *t*-Butyl Alcohol Solutions^{1,2}

Sir:

We wish to report an enormous change in the heat of solvation resulting from a modest composition change in a highly aqueous alcohol solution. The partial molal heat of solution at infinite dilution ($\Delta\bar{H}_s$) of crystalline sodium tetraphenylboride in pure water is -5.2 ± 0.1 kcal./mole, while that in water containing only 0.045 mole fraction of *t*-butyl alcohol is 11.7 ± 0.1 kcal./mole. The difference of nearly 17 kcal./mole produced by adding this small amount of a hydroxylic cosolvent to water occurs at a sharp maximum (Figure 1) and may very well have implications for a number of areas of physical and biological chemistry.

Many properties of water-alcohol solvent systems go through sharp maxima in water-rich regions of the solvent spectrum. These facts have been reviewed recently by Franks³ and interpreted in terms of an increase (*sic*) in the structuredness of the solvent occasioned by the first increments of added cosolvent; larger quantities eventually cause the expected disruption of solvent structure. *t*-Butyl alcohol is especially inter-

(1) Solvent Effects in Organic Chemistry. VI. Contribution 1265 from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa. 15213.

(2) This research was made possible through a grant provided by the National Science Foundation (G-14583 and GP-2014).

(3) F. Franks, *Quart. Rev.* (London), in press. We are grateful to Professor Franks for helpful discussions and allowing us to use his manuscript.

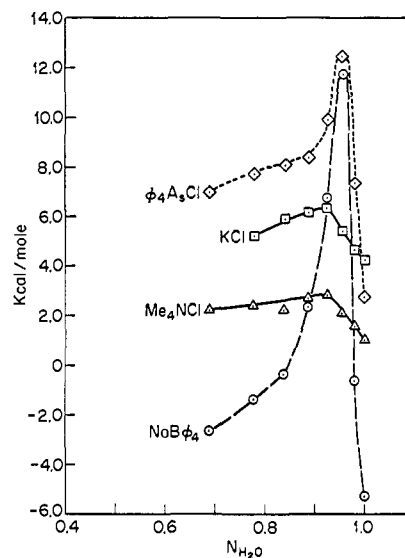


Figure 1. Partial molal heats of solution at infinite dilution ($\Delta\bar{H}_s$) for several electrolytes in aqueous *t*-butyl alcohol solutions. The curve for tetraphenylarsonium chloride refers to its dihydrate. On the basis of our results in aqueous ethanol, the curve for the anhydrous salt will be identical with this, although slightly displaced in an exothermic direction.

esting for such studies because at room temperature its miscibility is just on the borderline of allowing a complete spectrum of binary solvent mixtures. Tommila⁴ and co-workers have given particular attention to aqueous solutions of this alcohol and find that extrema for molal volumes, heats of mixing, and deviations from Raoult's law are generally larger than for aqueous solutions of lower alcohols and occur at higher water concentrations (on the mole fraction scale). The same may be said for ultrasonic absorption,⁵ an important guide to solvent structure, and the solvent effect on enthalpy of activation.⁶

The measurements of Moss and Wolfenden⁷ and Slansky⁸ for partial molal heats of solution of various low molecular weight salts in aqueous methanol also exhibit small endothermic maxima about 0.80 mole fraction of water, and recent measurements from this laboratory^{9,10} show clearly that in water-ethanol mixtures a number of salts and nonelectrolytes of varying molecular size give endothermic maxima (relative to water) for $\Delta\bar{H}_s$ in solutions of the same composition where physical properties³⁻⁵ and heats of activation^{6,11} pass through maxima or minima. Of more importance is the fact that the size of the maximum is roughly proportional to the size of the molecular (or ionic) particles of the solute, an extreme case being sodium tetraphenylboride, which gives a maximum (relative to its value in water) of 10.7 kcal./mole in a solution of 0.88 mole fraction of water. The above facts immediately

(4) J. Kenttamaa, E. Tommila, and M. Martin, *Ann. Acad. Sci. Fennicae, AII.*, No. 93 (1959).

(5) W. G. Schneider, *Colloq. intern. centre natl. rech. sci.* (Paris), 77, 529 (1959).

(6) J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, 34, 931 (1956).

(7) R. L. Moss and J. H. Wolfenden, *J. Chem. Soc.*, 118 (1939).

(8) C. M. Slansky, *J. Am. Chem. Soc.*, 62, 2430 (1940).

(9) E. M. Arnett, P. M. Dugleby, and J. J. Burke, *ibid.*, 85, 1350 (1963).

(10) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Dugleby, *ibid.*, in press.

(11) S. Winstein and A. H. Fainberg, *ibid.*, 79, 5937 (1957).