TABLE I

ASSOCIATION CONSTANTS, K_1 (MOLES/MOLE OF SOLVENT)$^{-1}$, OF $CdBr^+$ AND SPECIFIC HELMHOLTZ FREE ENERGIES OF ASSOCIATION, $-\Delta A$ (KCAL/MOLE), IN MIXTURES OF $LiNO_3$, $NaNO_3$, AND KNO_3; $Z = 6$

Solvent, mole %					
KNO_3	$NaNO_3$	$LiNO_3$	T, °C	K_1	$-\Delta A$
100	0	0	358	650	5.88[a]
0	100	0	331	625	5.58[a]
0	0	100	...	....	6.87[b]
50	50	0	240	1520	5.67[c]
50	50	0	258	$1500\begin{cases}+0\\-100\end{cases}$	$5.83\begin{cases}+0^a\\-0.07\end{cases}$
50	50	0	300	990	5.83[c]
0	50	50	240	2700	6.23[d]
74	0	26	240	2300	6.06[e]
60	0	40	240	2650	6.20[e]
50	0	50	240	3200	6.38[e]
35	0	65	240	3600	6.58[e]
20	0	80	240	4200	6.67[e]
50	0	50	171	8000	6.33[e]

[a] See ref 2. [b] Least-squares value; see also ref 4. [c] See ref 3. [d] This work. [e] See ref 4.

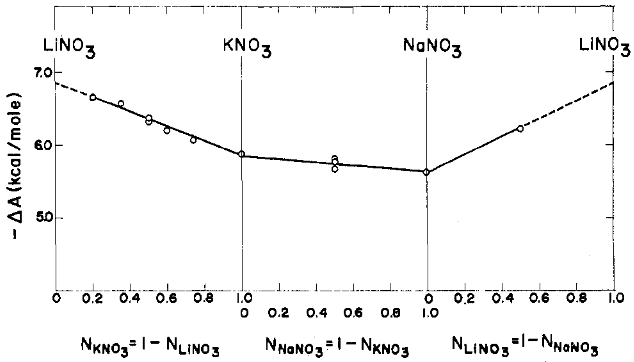

Figure 2.—Variation of the specific Helmholtz free energy of formation of $CdBr^+$ in mixtures of $LiNO_3$, KNO_3, and $NaNO_3$. The points are calculated from the measured association constants, and the lines were determined by a least-squares fit of the points.

are 5.85 ± 0.04, 5.61 ± 0.04, and 6.87 ± 0.05 kcal/mole. These results agree, within ±0.03, with the values which are accessible by direct measurement and with the value of ΔA in $LiNO_3$ estimated previously from results in mixtures only of $LiNO_3$ and KNO_3.

From the differences of the values of the specific Helmholtz free energies of association in Table I, we find the solvent effect: $\Delta A_{Na} - \Delta A_K = 0.29$ kcal/mole (destabilization of $CdBr^+$ in $NaNO_3$ relative to KNO_3) and $\Delta A_{Li} - \Delta A_K = -0.99$ kcal/mole (stabilization in $LiNO_3$ relative to KNO_3). These differences may be compared with the differences of the coulombic energy of exchange of nearest neighbor ions (*i.e.*, the "reciprocal coulomb effect")[4,8,9] in the association reactions

$$CdNO_3^+ + KBr = CdBr^+ + KNO_3 \qquad \Delta U_K$$

$$Cd(NO_3)^+ + LiBr = CdBr^+ + LiNO_3 \qquad \Delta U_{Li}$$

$$Cd(NO_3)^+ + NaBr = CdBr^+ + NaNO_3 \qquad \Delta U_{Na}$$

The differences are more nearly consistent with a smaller "effective radius" of nitrate ion than the value 2.19 A assumed previously.[4] Kapustinskii[10] has suggested the value 1.89 A for the "thermochemical" radius of nitrate ion. We have reported[4,11] that the solvent effect (stabilization in $LiNO_3$ and destabilization in $NaNO_3$) indicates a smaller "effective radius" of nitrate ion in lithium nitrate than in the other alkali nitrates. Meschel and Kleppa later reported that their thermochemical data indicate a nitrate ion "effective radius" of 1.93 A in typical fused nitrates and 1.85 A in lithium nitrate.[12] In the present work, the solvent effect would be in agreement with the calculated reciprocal coulomb effect with a nitrate ion radius or "distance of closest approach" of 1.98 A in sodium nitrate and potassium nitrate and 1.94 A in lithium nitrate. Such correlations may be useful in predicting solvent effects on association equilibria but must be recognized as empirical since the change of coulombic energy due to ions other than nearest neighbors, as well as the effects of polarization and dispersion, are not considered in the simple calculations of the reciprocal coulomb effect.

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(8) D. L. Manning, R. C. Bansal, J. Braunstein, and M. Blander, *J. Am. Chem. Soc.*, **84**, 2028 (1962).

(9) J. Braunstein and J. D. Brill, *J. Phys. Chem.*, **70**, 1261 (1966).

(10) A. F. Kapustinskii, *Quart. Rev.* (London), **10**, 283 (1956)

(11) The following corrections to ref 4, which do not alter the conclusions, should be noted. The second term in the bracket on the right of eq 1 should read $1/(r_B + r_X)$, without a prime. The subscripts $LiNO_3$ and KNO_3 in the equation for $-\Delta A_{CdBr^+}$ under the graph in Figure 3 are reversed. The numerical values calculated for β, α, and Δ in the last paragraph should read −0.20, −0.068, and −0.028 (instead of −0.16, −0.053, and −0.018), respectively, and the decrease in the distance of closest approach which would reverse the sign of the calculated $\Delta(\Delta U)$ should read 0.10 instead of 0.08.

(12) S. V. Meschel and O. J. Kleppa, *J. Phys. Chem.*, **68**, 3840 (1964).

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Alcoholysis of $(CF_3P)_n$ Rings. A Volatile Open-Chain Tetraphosphine[1]

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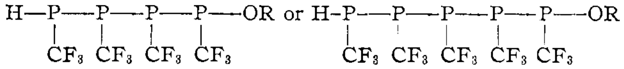
Alcohols cleave a P–P bond in $(CF_3P)_4$ or $(CF_3P)_5$,[2] evidently forming first a full-length open chain



$$H-\underset{CF_3}{P}-\underset{CF_3}{P}-\underset{CF_3}{P}-\underset{CF_3}{P}-OR \text{ or } H-\underset{CF_3}{P}-\underset{CF_3}{P}-\underset{CF_3}{P}-\underset{CF_3}{P}-\underset{CF_3}{P}-OR$$

The relatively electronegative F_3CPOR end group could be expected to attract basic invasion (by O of ROH) more effectively than other P atoms in the chain, and indeed scarcely less effectively than P in the original rings. In fact, a secondary alcoholysis begins long before the first step is complete and gives higher yields of $CF_3P(OR)_2$ and the open-chain polyphosphine $H_2(CF_3P)_{n-1}$ than random P–P cleavage could account for. Thus, we have a relatively convenient and efficient method of making the triphosphine $H_2(CF_3P)_3$;[2] and by

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(2) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

a special procedure it is possible to show that the alcoholysis of $(CF_3P)_5$ produces the previously unknown and even less stable tetraphosphine $H_2(CF_3P)_4$.

Methanolysis of the Tetramer.—A mixture of 1.085 mmoles of $(CF_3P)_4$ and 3.15 mmoles of CH_3OH, in a vertical tube attached to a high-vacuum manifold, showed effervescence below 0°. After 12 hr at 25°, the mixture was resolved into the following fractions:

1. CF_3PH_2...0.029 mmole (47 mm at −78°)
2. "$CF_3PH(OCH_3)$"...0.134 mmole (166 mm at 0°; mol wt 130.5 *vs.* calcd 132; basic hydrolysis gave 0.51HCF_3 per mole, as expected in view of 2.5HCF_3 per mole of the CF_3P pentamer[2])
3. $\left\{\begin{array}{l}(CF_3PH)_2\ldots 0.176\text{ mmole}\\ CH_3OH\ldots 0.167\text{ mmole}\end{array}\right\}$ inseparable but proved by analysis
4. $\left\{\begin{array}{l}\text{“}CF_3HP\text{–}PCF_3(OCH_3)\text{”}\ldots 35\%\\ CH_3P(OCH_3)_2\ldots\ldots\ldots\ldots 54\%\\ CH_3OH\ldots\ldots\ldots\ldots\ldots\ldots 11\%\end{array}\right.$
   (Roughly one-third of the whole mixture; mole per cents estimated from average molecular weight and HCF_3 yield from basic hydrolysis)
5. $H_2(CF_3P)_3$...roughly 0.5 mmole (3.5 mm at 0°)
6. Products nonvolatile at 25°

Thus, the recoverable yield of the triphosphine was almost 50%, even though some of it may have been attacked by the excess methanol. The new compound "$CF_3PH(OCH_3)$" was well indicated but not further characterized, while the new diphosphine "CF_3HP–$PCF_3(OCH_3)$" is only reasonably postulated.

The Tetramer with Ethylene Glycol.—A solution of 1.860 mmoles of $(CF_3P)_4$ and 1.875 mmoles of $C_2H_4(OH)_2$ in tetralin was heated for 15 hr at 100° (required temperature) under 225 mm of dry nitrogen, with delivery of volatiles at intervals through the reflux region of the vertical reaction tube. The effluent was resolved into 0.02 mmole of HCF_3, 0.103 mmole of CF_3PH_2, 0.031 mmole of $(CF_3PH)_2$, 0.70 mmole of $H_2(CF_3P)_3$ (50% yield, based upon consumed tetramer), 1.4 mmoles of a fraction seeming to be mostly $C_2H_4O_2PCF_3$,[3] and 0.176 mg (24% recovery) of $(CF_3P)_4$.

The glycol ester stood some 5 weeks at or below 25°, converting almost wholly to a nonvolatile viscous liquid which could represent more than one possible kind of polymerization.

Characterization of the Triphosphine.—The above alcoholyses led to pure samples of $H_2(CF_3P)_3$, for which the volatility data of Table I were obtained.

TABLE I

VAPOR TENSIONS OF LIQUID $H_2(CF_3P)_3$[a]

Temp, °C	0.0	16.9	22.6	29.9	36.4	42.9
P_{obsd}, mm	3.5	10.3	14.5	21.5	30.1	41.3
P_{calcd}, mm	3.6	10.4	14.4	21.5	30.04	41.3

[a] $\log P = 6.4627 + 1.75 \log T - 0.0054T - 2375/T$; t_{760} = 187.7°; Trouton constant = 21.3 eu.

This triphosphine is appreciably unstable in the presence of mercury, tending to form $(CF_3P)_n$ and the diphosphine $(CF_3PH)_2$. It decomposes far more rapidly in the presence of a phosphine base. Thus, with a 10% admixture of $(CH_3)_3P$, the following millimolar stoichiometry was observed.

$$\begin{array}{llll} H_2(CF_3P)_3 & \longrightarrow H_2(CF_3P)_2 & + (1/n)(CF_3P)_n & (\text{fast at } 25^\circ) \\ \quad 0.048 & \qquad 0.042 & \qquad 0.044 & \\ \underline{-0.004} & & & \\ \quad 0.044 & & & \end{array}$$

Such catalysis correlates with the formation of the monomer complex $(CH_3)_3PPCF_3$.[4]

Alcoholysis of the Pentamer.—The instability of $H_2(CF_3P)_3$ relative to $H_2(CF_3P)_2$ suggested that the similar tetraphosphine would be even less stable. In order to obtain it directly in pure form, it seemed well to attack $(CF_3P)_5$ with a long-chain alcohol, so that both this alcohol and any alkoxyphosphine byproducts would be less volatile than the desired tetraphosphine; then this product could be obtained as a certain fraction in a distillation process. In fact, exploratory experiments had shown that methyl, *t*-butyl, and *n*-heptyl alcohols all attacked $(CF_3P)_5$ well enough but formed mixtures from which the desired tetraphosphine could not be isolated; however, the problem was solved by the use of *n*-dodecyl alcohol (lauryl alcohol). This attacked $(CF_3P)_5$ at 30–40° (during 6 hr) in the boiler bulb of a small fractionating column (operating *in vacuo* with reflux at −15°), delivering a fraction which passed through a U tube at −23° and condensed in a second trap at −45°—through which the more volatile products were removed. The vacuum-line stopcocks were halocarbon-greased to minimize catalytic effects.

The volatility of the −45° condensate was 5 mm at 25°, reasonably higher than that of the solid $(CF_3P)_4$ or liquid $(CF_3P)_5$. The apparent molecular weight of the nearly saturated vapor was 424 (calcd for the chain tetraphosphine, 402); and subsequent measurements showed lower and lower results as decomposition increased the number of molecules. A long process of catalytic decomposition of a 25.6-mg repurified sample (from which the chain triphosphine might not have been quite absent) gave 0.054 mmole of CF_3PH_2, 0.151 mmole of CF_3P as tetramer and pentamer, and 0.018 mmole of $(CF_3PH)_2$. Thus, the formula could be written empirically as $H_{2.15}(CF_3P)_{3.78}$, representing a reasonable confirmation of the formula $H_2(CF_3P)_4$.

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(3) A. B. Burg and J. E. Griffiths, *J. Am. Chem. Soc.*, **83**, 4333 (1961).

(4) A. B. Burg and W. Mahler, *ibid.*, **83**, 2388 (1961).

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Preparation of Cobalt(III) Complexes by Continuous Anodic Oxidation

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Complexes of Co(III) have been prepared from aqueous Co(II) solutions in various ways. Most fre-