more than compensates for the diminished hydrogen bonding. Interestingly, the larger K values appear to be due in greater part to less negative entropy values rather than more negative enthalpy values. This suggests that, in part at least, the increase in K values over the ether is related to the larger sulfur atom being more accessible to the acceptor sites.

When more than one type of complex is possible with a given acceptor, the experimental association parameters are difficult to interpret. In an attempt to sort out the various types, *i.e.*, to resolve the "mixed" association constants into the individual contributions from the various types of complexes, the tetrahalomethanes, CCl_4 and CBr_4, were studied. The results for these systems do provide evidence of complex formation stabilized by some type of halogen–n-donor interaction. The trends are as expected, the smallest K value being obtained for the CCl_4–ether system and the largest for the CBr_4–thioether system. However, the values of K and ΔH obtained for the CBr_4–thioether system preclude any detailed quantitative treatment of the data. Taking them at face value the data indicate that H bonding in the $CHBr_3$–thioether system is negligible and that the bulk of the association constant is largely due to charge transfer. Spectroscopic evidence indicates that this is not the case. Hydrogen bonding should still provide a significant contribution to the overall K measured for the $CHBr_3$–thioether complex. Thus it does not appear to be a valid assumption that a quantitative estimate of the charge-transfer contribution in the haloforms could be obtained from the tetrahalomethane data. Further investigation of the $-CCl_3$ group by studying the solute 1,1,1-trichloroethane yielded interesting results. The K values were fairly small in absolute terms but were larger than those for CCl_4 and the ΔH's were sizable with the haloalkane–ether having a value of $\sim$1.8 kcal mol^{-1}. This ΔH is comparable to that observed for the weak hydrogen-bonded complexes involving the haloforms with thioether and gives an indication of the magnitude of dipolar interactions in mixtures of polar liquids.

The importance of classical electrostatic interactions in the stabilization of weak "collision complexes" has been emphasized in recent publications.[45,48] It is indeed possible that a significant contribution to the stabilization of some of the complexes discussed in this paper is due to dipole–dipole and/or dipole–induced dipole interactions. Bromine is a better charge-transfer acceptor atom than chlorine but it is also a good deal more polarizable. Thus the trend of increasing K values with increasing Br substitution follows the increasing degree of polarizability of the haloform. However, concomitantly with this the C–Cl bond dipoles of the remaining C–Cl bonds are increased due to Br substitution. It is possible that these bond dipoles could interact with the positive end of the ether dipole thus affording another site for interaction. The dipole moment of the thioether is somewhat larger than that of the ether and this could possibly account for some of the increase in K values in the haloalkanes on going from the ether to the thioether. However, that effect alone could hardly explain the large increases in the bromoform and carbon tetrabromide K values. Thus it would appear that while the trends in the K values could be approximately explained by electrostatic considerations, the possibility that all of these types of interactions could contribute in part to the average values of K observed by glc makes it impossible to resolve these values into their most significant contributions. It has been observed[48] that nmr is an experimental method which also averages over many "dipolar" contributions while ir would not show these effects in a direct way. Work is currently underway in this area which may throw further light on the nature of these interactions at the molecular level.

Acknowledgment. This research was supported by a grant from the National Science Foundation.

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(48) M. D. Johnston, Jr., F. P. Gasparro, and I. D. Kuntz, Jr., *J. Amer. Chem. Soc.*, 91, 5715 (1969).

Thermodynamics of Molecular Association by Gas–Liquid Chromatography. III. Aromatic Compounds with Tetra-*n*-butyl Pyromellitate

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Abstract: Equilibrium constants, enthalpies, and entropies of complex formation between benzene, toluene, the xylenes, and mesitylene and tetra-*n*-butyl pyromellitate have been determined by gas–liquid chromatography in the temperature range 50–80°. Steric effects were found to predominate over electronic factors leading to the trend benzene > toluene > *o*-xylene > *p*-xylene > *m*-xylene > mesitylene for the equilibrium constants.

It is now generally recognized that gas–liquid chromatography (glc) is an effective and advantageous method for studying the thermodynamics of nonelectrolytic solutions. The most recent application is to the accurate and rapid measurement of association constants of organic complexes in nonaqueous solution. A classification system has been suggested[1] for the various more probable experimental approaches. Recently, two such approaches were independently developed and utilized.

Martire and Riedl[2] proposed a quantitative glc method [class B (ii) according to Purnell[1]] for study of hydrogen bonding. It employs two columns, one containing the electron-donor liquid phase and the other a "reference" alkane liquid phase of approximately the same molecular size, shape, and polarizability as the electron donor.[3] Association constants, enthalpies, and entropies of hydrogen-bond formation were obtained for eight alcohols with di-*n*-octyl ether and di-*n*-octyl ketone; the reference alkane was *n*-heptadecane. More recently,[4] this method was used to study the association (hydrogen bond and charge transfer) of various haloalkanes with di-*n*-octyl ether and di-*n*-octyl thioether.

Cadogan and Purnell[5] measured the formation constants of, and thermodynamic parameters for, complexes formed between benzene, toluene, and the xylenes and di-*n*-propyl tetrachlorophthalate. Their method [class A (ii) according to Purnell[1]] necessitates the use of several columns (six or seven) containing different concentrations of the additive (electron acceptor in this case) in an inert solvent. Recently, they utilized this approach for the quantitative evaluation of hydrogen-bond formation constants for several alcohols with didecyl sebacate[6] (the additive). In both studies the inert solvent used was squalane.

Partly to familiarize ourselves with the Cadogan–Purnell method, but mainly to initiate a glc investigation of our own on aromatic–aromatic complexes, we undertook the present study. Struck by the strong electron-acceptor properties of pyromellitic dianhydride,[7] we decided on and synthesized its tetra-*n*-butyl ester (chosen to impart a low vapor pressure and to promote solubility in the inert paraffinic solvent) for this initial study.

Cadogan–Purnell Method[5]

Consider a volatile solute X reacting with an additive A which is dissolved in an unreactive solvent S. Assuming the formation of 1 : 1 complexes only, we have

$$\begin{gathered} X(g) \overset{K_R^0}{\rightleftharpoons} X(l) \\ X(l) + A(l) \overset{K_1}{\rightleftharpoons} AX(l) \end{gathered} \qquad (1)$$

where K_R^0 is the partition coefficient of uncomplexed X between S and the gas phase and K_1 is the thermodynamic formation constant of AX in S. Since both AX(l) and X(l) will be infinitely dilute solutions of S under the conditions of the glc experiment, with the convention that $a_i \rightarrow c_i$ as $c_i \rightarrow 0$, we have

$$K_1 = c_{AX}/c_X a_A \qquad (2)$$

The apparent gas-chromatographic partition coefficient, K_R, assuming no volume change on dissolution of X and ideal behavior of A in S (*i.e.*, $a_A = c_A$ or $\gamma_A = 1$ for all concentrations of A in S), is then given by[1,5]

$$K_R = K_R^0(1 + K_1 c_A) \qquad (3)$$

where c_A is the additive concentration. K_R is evaluated from the fully corrected net peak maximum retention volume, V_R, through the familiar glc equation at infinite dilution of X

$$V_R = K_R V_L \qquad (4)$$

where V_L is the total volume of liquid phase (solvent plus additive) in the column.

Thus, from plots of K_R against c_A, constructed from measurements of V_R made on a series of columns containing different amounts of additive, both K_R^0 and K_1 may be evaluated. Linear behavior over the concentration range used would be a direct confirmation of the validity of the assumptions made.

Experimental Section

Liquid Phase. The potential electron acceptor and additive was tetra-*n*-butyl pyromellitate (TBPM). It was synthesized from pyromellitic dianhydride (the anhydride of 1,2,4,5-benzenetetracarboxylic acid) and 1-butanol using the method described by Langer, Zahn, and Vial.[8] The unreactive or inert solvent, squalane, was obtained from Applied Science Laboratories. High-temperature glc indicated no discernible impurities in the TBPM sample and a lower boiling trace impurity (less than 1%) in the squalane sample.[9] In order to employ eq 3 and 4 it is necessary to know the densities of the liquid phase at the experimental temperatures. These have been published for squalane[6] and were determined by pycnometry for TBPM. The data are given in Table I.

Table I. Densities (g/ml) of Solvent and Additive

	50.0°	60.0°	70.0°	80.0°
Squalane	0.789	0.783	0.777	0.771
TBPM	1.047	1.039	1.032	1.024

Preparation of Columns. The solid support material used was Johns-Manville Chromosorb W, 60–80 mesh, acid-washed and DMCS treated. The liquid phase was coated onto the support material in a rotary evaporator from a solution of carefully weighed amounts of TBPM and squalane in methylene chloride. Six different coatings were made; each contained close to 10%, by weight, liquid phase. The exact liquid weight percentages were determined by a combustion or ashing method.[2] Assuming additivity of volumes on mixing, the concentration of additive, c_A, in the liquid phase was determined for each of the six coatings with the use of Table I. Summarized in Table II are the TBPM concentrations

Table II. Concentrations of Additive (mol/l.)

Coating	50.0°	60.0°	70.0°	80.0°
1	0	0	0	0
2	0.212	0.210	0.208	0.207
3	0.299	0.296	0.294	0.291
4	0.390	0.387	0.383	0.380
5	0.478	0.474	0.471	0.467
6	0.554	0.549	0.545	0.540

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[1] J. H. Purnell, "Gas Chromatography," A. B. Littlewood, Ed., Elsevier, Amsterdam, 1966, p 3.

[2] Paper I in this series: D. E. Martire and P. Riedl, *J. Phys. Chem.*, 72, 3478 (1968).

[3] Since experiments on a single unadulterated column cannot yield association constants directly,[1] a reference column must be used for evaluation of the nonspecific interactions between the electron donor and hydrogen donor.

[4] Paper II in this series: J. P. Sheridan, D. E. Martire, and Y. B. Tewari, *J. Amer. Chem. Soc.*, **94**, 3294 (1972).

[5] D. F. Cadogan and J. H. Purnell, *J. Chem. Soc. A*, 2133 (1968).

[6] D. F. Cadogan and J. H. Purnell, *J. Phys. Chem.*, 73, 3849 (1969).

[7] L. L. Ferstandig, W. G. Toland, and C. D. Heaton, *J. Amer. Chem. Soc.*, 83, 1151 (1961).

[8] S. H. Langer, C. Zahn, and M. H. Vial, *J. Org. Chem.*, **24**, 423 (1959).

[9] A sample of May and Baker "Embaphase" brand of squalane showed a much larger trace impurity (greater than 1%) in our high-temperature glc scan.

Table III. Values of K_R^0 (Squalane) and the Association Constant K_1 (l. mol^{-1})

	50°	60°	70°	80°
		K_R^0 Values		
Benzene	208.5	153.3	114.8	88.0
Toluene	601.8	418.7	297.5	215.4
o-Xylene	2025	1331	896.9	617.6
m-Xylene	1722	1129	758.0	520.6
p-Xylene	1682	1105	744.0	512.2
Mesitylene	4751	2954	1889	1239
		K_1 Values		
Benzene	0.494 ± 0.011	0.453 ± 0.010	0.416 ± 0.013	0.399 ± 0.019
Toluene	0.461 ± 0.015	0.434 ± 0.018	0.393 ± 0.010	0.390 ± 0.009
o-Xylene	0.483 ± 0.005	0.428 ± 0.018	0.384 ± 0.021	0.367 ± 0.006
m-Xylene	0.390 ± 0.010	0.365 ± 0.013	0.349 ± 0.011	0.361 ± 0.010
p-Xylene	0.410 ± 0.014	0.385 ± 0.011	0.353 ± 0.019	0.361 ± 0.011
Mesitylene	0.378 ± 0.019	0.336 ± 0.023	0.309 ± 0.018	0.304 ± 0.014

at the four experimental temperatures. The coated support was packed into 0.25-in. o.d. copper tubing. Column lengths of 4.5–5 ft were used for the moderate retention time compounds and lengths of about 2.5 ft for the long retention time ones.

Solutes. The potential electron donors selected for this study were benzene, toluene, *o*-, *m*-, and *p*-xylene, and mesitylene. Since solute purity is not an important consideration in these studies, all solutes were used without further purification.

Apparatus and Procedure. The glc apparatus used in this work is described elsewhere.[2] For the present study the detector block temperature was held at about 250° and the injection port temperature at about 200°. The column bath temperature was controlled and measured to within ±0.05°. The general procedure used for obtaining meaningful and accurate net retention volumes is also described elsewhere.[10] No evidence was found for solute adsorption at either the gas–liquid or solid–liquid interface for the systems studied here.

Results

The net retention volume was determined for each solute with each of the six columns at 50.0, 60.0, 70.0, and 80.0° from the average value of three separately measured retention times. Apparent partition coefficients, K_R, were calculated from eq 4 and the values plotted against c_A for all six solutes. There was no indication of deviation from linear behavior for any of the systems; the linear correlation coefficients were all in excess of 0.999. This confirms the validity of eq 4 with K_1 representing a thermodynamic (as opposed to stoichiometric) equilibrium constant for a 1:1 complex. In order to establish that the linear dependence of K_R on c_A does not stem from mixed solvency effects, experiments were conducted at 70.0° with cyclohexane, a solute most unlikely to complex with TBPM. A least-squares treatment of the data yielded a K_R which was essentially independent of c_A ($K_R \approx K_R^0 = 142.6 \pm 0.5$) and a line slope corresponding to a K_1 of merely 0.009 l. mol^{-1}, which is within the probable error.

Listed in Table III are the derived values of K_R^0 (squalane), K_1, and the standard deviation in K_1 at the four experimental temperatures. The standard deviations represent a range of probable error in $\Delta G°$ (*i.e.*, $-RT \ln K_1$) of from ±5 cal mol^{-1} for the best measurement (*o*-xylene at 50°) to ±35 cal mol^{-1} for the worst measurement (mesitylene at 60°), with a typical value being less than ±20 cal mol^{-1} (in good agreement with the statistical estimate of ±25 cal mol^{-1} given by Cadogan and Purnell[5]). The *actual* K_R^0 values measured with pure squalane columns are listed; these data differ by, on the average, 0.4% from the values obtained from the intercepts of plots of K_R against c_A. For consistency, the actual values were used in the computation of K_1 from the slopes.

A comparison of fully corrected infinite-dilution solute activity coefficients (γ_f^∞) in pure squalane at 70.0° is given in Table IV. The equations and pure component physical data used in determination of γ_f^∞ from K_R^0 are given elsewhere.[5] Locke's results represent values interpolated from a detailed survey and assessment of the available data for these systems for the range 25–135°.

Table IV. Comparison of Infinite-Dilution Solute Activity Coefficients (γ_f^∞) in Squalane at 70.0°

	Ref 5	Locke[a]	This work[b]
Benzene	0.629	0.640	0.638
Toluene	0.657	0.662	0.659
o-Xylene	0.690	0.696	0.698
m-Xylene	0.683	0.696	0.692
p-Xylene	0.667	0.686	0.679

[a] These values were cited in ref 5 as a personal communication from D. C. Locke. [b] Computed from the K_R^0 values in Table III and the equations and pure component physical data given in ref 5.

Since

$$-R \ln K = \Delta H°/T - \Delta S° \tag{5}$$

the thermodynamic parameters $\Delta H°$ and $\Delta S°$ are readily obtainable from the K_1 data in Table III. The derived values of $\Delta H°$ and $\Delta S°$ are listed in Table V along with their standard deviations. A clearer picture of the goodness of fit can be seen in Figures 1–3 where the data points for K_1, their corresponding standard deviations, and the least-squares best fit straight lines are illustrated.

Table V. Enthalpies (kcal/mol) and Entropies (eu) of Complex Formation with TBPM

	$-\Delta H°$	$-\Delta S°$
Benzene	1.65 ± 0.15	6.50 ± 0.37
Toluene	1.39 ± 0.25	5.84 ± 0.65
o-Xylene	2.12 ± 0.25	8.05 ± 0.63
m-Xylene	0.64 ± 0.36	3.90 ± 0.92
p-Xylene	1.07 ± 0.36	5.11 ± 0.91
Mesitylene	1.69 ± 0.34	7.20 ± 0.88

(10) Y. B. Tewari, D. E. Martire, and J. P. Sheridan, *J. Phys. Chem.*, 74, 2345 (1970).

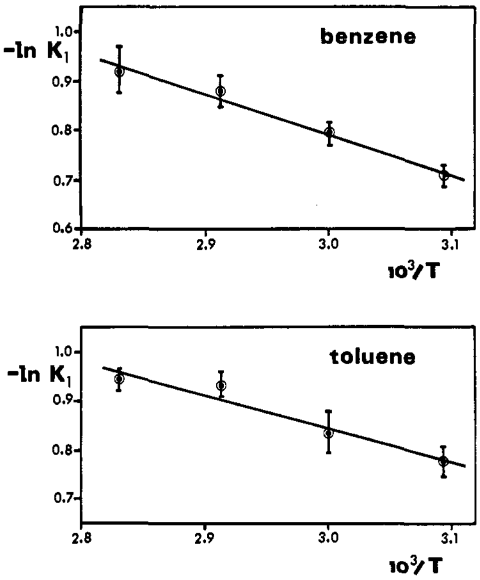

Figure 1. Temperature dependence of the association constant (K_1).

Discussion

It is apparent from the trend in K_1 (roughly, benzene > toluene > *o*-xylene > *p*-xylene > *m*-xylene > mesitylene) that steric hindrance is playing an important role in these systems. The out-of-plane ester groups of the TBPM are preventing closeness of approach of the aromatic "donors," thus impeding the formation of coplanar complexes. In the absence of steric factors, electronic effects alone should produce the following trend in K_1: mesitylene > *o*-xylene > *p*-xylene > *m*-xylene > toluene > benzene. The fact that the reverse trend is observed is a clear indication of steric opposition to and predominance over electronic factors.[11] This results in the small K_1 and $-\Delta H^\circ$ observed. Considering the exceptionally strong acceptor properties of pyromellitic dianhydride[7] (a better acceptor than tetracyanoethylene[7,11,12]), steric hindrance must be particularly pronounced in these systems. A survey of some available association constants for aromatic–aromatic complexes[11–13] indicates that, in comparing them to our values extrapolated to 25°, TBPM is a better "acceptor" than benzoquinone, a comparable one to picric acid and tetrachlorophthalic anhydride, a weaker one than *s*-trinitrobenzene, and a far weaker one than either pyromellitic dianhydride (PMDA) or tetracyanoethylene (TCNE).

We have avoided using the terms electron donor–acceptor complexes, $\pi \rightarrow \pi^*$ complexes, and charge-transfer complexes in describing our systems for a good reason. With PMDA strong charge-transfer bands were observed in solution with a variety of aromatic donors. Of those tried, all aromatic compounds with alkyl electron-donating substituents showed bands. However, we have not been able to observe a charge-transfer band for even the benzene–TBPM system. Perhaps, this is an indication that the band is weak and/or that it has been shifted to a shorter wavelength due to steric effects, or possibly that there is no band at all. In consideration of this latter point we decided to look at the spectra of solutions of tetramethylpyromellitate (TMPM) with aromatic donors. It is possible that the strong electron-acceptor properties of PMDA are due in part to the coplanarity of the anhydride groups with the benzene ring. In this case simple esterfication of the anhydride groups irrespective of chain length would largely destroy the electron acceptor properties because the carbonyl groups would be removed from their coplanar configuration with the ring and hence lose a great deal of their electron-withdrawing power. Therefore, solutions of TMPM in aromatic solvents were scanned in the uv-visible region of the spectrum. In every case new bands were observed which could be ascribed to charge-transfer excitation. However, the bands were found to be blue shifted with respect to those observed for the PMDA complexes. In fact, in most cases the bands were considerably over-

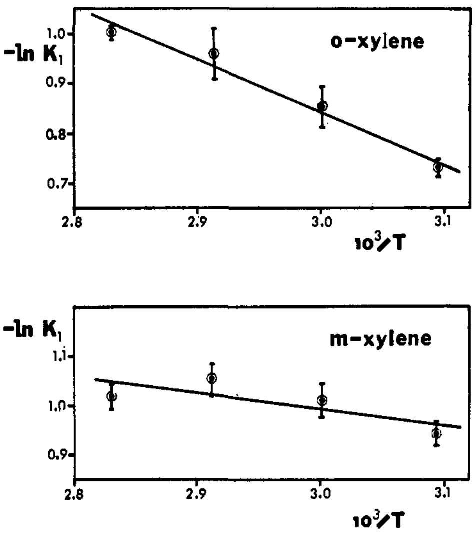

Figure 2. Temperature dependence of the association constant (K_1).

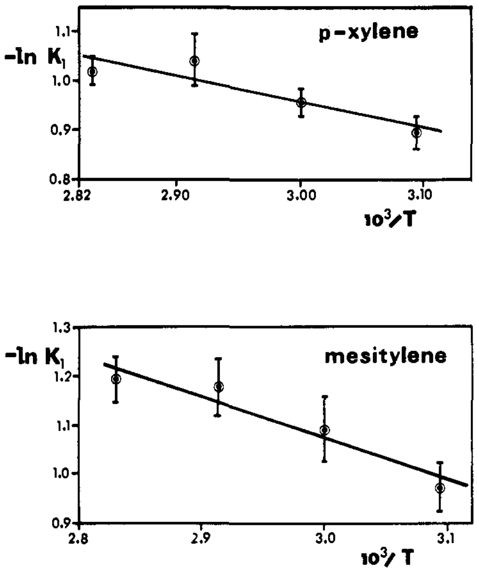

Figure 3. Temperature dependence of the association constant (K_1).

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(11) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964.

(12) P. H. Emslie, R. Foster, I. Horman, J. W. Morris, and T. R. Twiselton, *J. Chem. Soc. B*, 1161 (1969), and references and results contained therein.

(13) L. J. Andrews, *Chem. Rev.*, **54**, 713 (1954).

lapped by the ester, a fact which would make it very difficult to carry out a quantitative spectroscopic study. However, we can say qualitatively that esterification *per se* does not destroy the acceptor properties of the pyromellitic moiety although complexes formed by TMPM would be expected to be weaker than those formed by PMDA since the charge-transfer absorption bands were found to be further into the uv than those of PMDA. Thus, it would appear that, from an electronic point of view, TBPM should display acceptor properties and that the trends observed with increasing methyl substitution in this study are indeed wholly steric in origin.

The presence of a band is, at the very least, evidence that charge-transfer interaction is contributing to the overall molecular interaction between unlike species. However, it is not conclusive proof that a complex exists or that, if it does exist, charge-transfer interaction is the main stabilizing force in the complex formation.[14] On the other hand, the absence of a band (or even a weak band), coupled with direct thermodynamic evidence that some sort of association is taking place, strongly suggests that "classical" electrostatic forces primarily are stabilizing the complex.[14] Even if bands did exist for our systems, it would be particularly difficult to partition the contributions of electrostatic and charge-transfer forces because of the direct correlation between the molecular polarizability and ionization potential within this series of aromatic donors.[12] Further glc and spectroscopic studies with the tetramethyl or tetraethyl esters of PMDA (the factors in the choice of ester group being those of volatility and solubility noted previously) may clear up some of the questions raised above and should provide additional insight into the steric and electronic effects operative in these systems.

Acknowledgment. This research was supported by a grant from the National Science Foundation. One of us (M. A. C.) is grateful to the National Science Foundation for support under the Undergraduate Research Participation Program. We also wish to thank Mr. George Janini for his assistance with the spectroscopic work.

(14) These points are discussed and references are given in ref 4.

Bistrifluoromethyl Peroxide. I. Thermodynamics of the Equilibrium with Carbonyl Fluoride and Trifluoromethyl Hypofluorite[1]

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Abstract: Equilibrium constants for the reaction $CF_3OOCF_3(g) \rightleftarrows COF_2(g) + CF_3OF(g)$ have been measured from 495 to 610°K. The standard enthalpies and entropies of reaction, corrected to 298°K, were found to be 24.5 ± 0.7 kcal mol^{-1} and 38.5 ± 1.2 gibbs mol^{-1}. These correspond to a standard heat of formation and a standard entropy at 298°K, for the peroxide, of -360.2 ± 3 kcal mol^{-1} and 97.0 ± 1.2 gibbs mol^{-1}. A bond dissociation energy of 40.6 ± 5 kcal mol^{-1} is calculated for the oxygen–oxygen bond in bistrifluoromethyl peroxide.

In 1957, Porter and Cady[2] reported that trifluoromethyl hypofluorite and carbonyl fluoride reacted at temperatures between 250 and 300° to give bistrifluoromethyl peroxide. Their results indicated that the reactants and product were in equilibrium with each other in this temperature range.

This result is an intriguing one, for most alkyl peroxides would be completely decomposed at much lower temperatures, *e.g.*, di-*tert*-butyl peroxide has a calculated half-life of about 0.7 sec at 250°.[3] The stability of CF_3OOCF_3 thus implies either an unusually strong oxygen–oxygen bond or a free energy balance between the peroxide and its products which favors the former.

The thermodynamic properties of CF_3OF and COF_2 are known,[5] but those of the peroxide are not. A study of the equilibrium constant for the reaction

$$CF_3OOCF_3 \rightleftarrows COF_2 + CF_3OF$$

as a function of temperature should yield information allowing the calculation of the heat content and entropy of the peroxide and lead to a resolution of the problem posed above.

The results of such a study are reported here. The results of a study of the reaction kinetics for this system will be reported soon.

Experimental Section

Chemicals. Bistrifluoromethyl peroxide, trifluoromethyl hypofluorite, and carbonyl fluoride were obtained from Peninsular Chem-Research and were used as received. Analysis by codistillation techniques[6] (see below) showed no evidence of impurities.

Apparatus and Procedures. The experiments were carried out in a 500-cm^3 spherical Monel vessel connected by 0.25-in. Monel tub-

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[1] This research was supported by Grant No. AFOSR 70-1939 of the Air Force Office of Scientific Research, Energetics Division.

[2] R. S. Porter and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 5628 (1957).

[3] Calculated from the rate expression given in ref 4.

[4] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

[5] "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1965.

[6] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).