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.

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[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).

ing to a Pace Model V7 pressure transducer. The pressure transducer sensing unit was a stainless-steel diaphram having a 0–250-mm range, and the signal was recorded on a chart automatically. A Hoke 482 M Monel valve connected the system to a small-volume Monel manifold used to evacuate and introduce samples to the vessel. The unheated volume was *ca.* 3 cm^3 and was neglected in the calculations. Passivation with elementary fluorine was tried but apparently produced a surface which catalyzed irreversible reactions which led to pressure increases exceeding a factor of 2. This was not investigated further. The procedure adopted was to carry out dissociations of peroxide samples at or below 350° until reproducible results were obtained. This generally took about four samples.

The vessel was maintained at the desired temperature by immersion in a thermostated bath of molten salts whose temperature was maintained to ±0.5°. Temperature readings were made using a calibrated chromel–alumel thermocouple. Equilibrium constants were determined by filling the vessel with a measured pressure of the peroxide at a known temperature and allowing equilibrium to occur. The standard procedure was to adjust the transducer scale so that the initial reactant pressure appeared at the 50% reading on the recorder chart. The procedure for determining the equilibrium pressure at some temperature involved taking a reading and then approaching the temperature of measurement from above and below. In every case, the pressures so determined agreed, within experimental error (see below). The temperature was then raised or lowered to a new level and the process repeated. From the deviation from the pressure calculated by the gas law, the composition and equilibrium constants were calculated.

The following tests were carried out to demonstrate the validity of the measurements. First, equilibrated samples were quenched from 280 to −196°, and the fact that the pressure dropped to zero was interpreted to rule out the presence of noncondensable products. Second, codistillation of a sample equilibrated at 280° showed only three components with retention times corresponding to those for CF_3OF, COF_2, and CF_3OOCF_3. Third, a similar equilibrum mixture was cooled to 170° slowly over a 3-day period and subjected to codistillation. Only CF_3OOCF_3 was found.

Finally, it may be noted that the consistency of the results obtained is also a good indication of the validity of the measurements.

Results

Four series of equilibrium constant measurements have been made. In three of these, the bulb was filled with pure bistrifluoromethyl peroxide and in the fourth series, the initial material was a mixture of the peroxide and carbonyl fluoride. The equilibrium constants so obtained are tabulated in Table I and plotted as the van't Hoff function in Figure 1. It is clear from the figure that the data obey the van't Hoff relation well and that the different series give results in good agreement with each other.

Table I. Equilibrium Constants for the CF_3OOCF_3, COF_2, CF_3OF System

Run I[a]		Run II[a]		Run III[a]		Run IV[a]	
Temp, °K	*K*, atm	Temp, °K	*K*, atm	Temp, °K	*K*, atm	Temp, °K	*K*, atm
495	0.0039	510	0.0063	490	0.0032	493	0.0033
515	0.0086	531	0.017	510	0.0067	532	0.020
535	0.022	550	0.041	523	0.012	552	0.045
573	0.095	570	0.089	534	0.021	572	0.098
595	0.20	591	0.18	554	0.048	595	0.21
612	0.36	611	0.36	557	0.057	615	0.42
		620	0.46	568	0.082	629	0.63
				578	0.11		
				581	0.12		
				592	0.20		
				599	0.23		
				601	0.25		
				607	0.34		
				616	0.41		
				623	0.57		
				625	0.50		

[a] The initial conditions for the above runs were: I, peroxide pressure measured at 220°, 18.1 Torr; II, peroxide pressure at 237°, 49.8 Torr; III, peroxide pressure at 308°, 145 Torr; IV, peroxide pressure 49.2 Torr, carbonyl fluoride pressure 21.8 Torr, both measured at 195°.

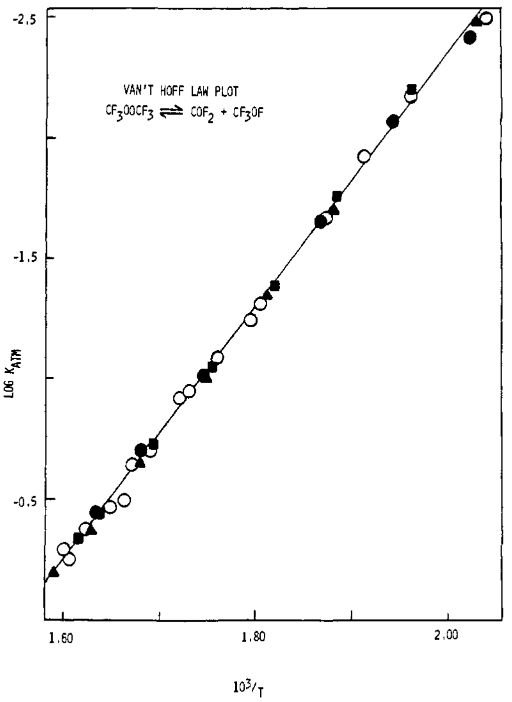

Figure 1. van't Hoff plot for the CF_3OOCF_3, CF_3OF, COF_2 equilibrium: (●) run I, (■) run II, (○) run III, (▲) run IV. (See Table I for conditions of each run.)

The precision of the equilibrium constant values is determined by the precision of the pressure measurements; *i.e.*, the effect of the ±0.5° temperature variation was considered negligible. Since for each series the recorder settings were such that the initial pressures approximately corresponded to a reading of 50% on the chart, and since the chart could be read to ±0.025%, the pressure differences, which were the actual parameters that were inserted into the equilibrium constant expression, were assigned probable errors of ±0.7% of the initial pressure.[7] The precision is thus determined by the pressure of the component present in least amount, and the equilibrium contents for mixtures which were largely dissociated or largely undissociated were hence subject to greater error than mixtures in between. Thus a mixture 90% dissociated (or associated) would have a 7% uncertainty. Mixtures dissociated to an extent of 50% would have errors of about 1.5%. It has thus seemed reasonable to assign an average probable error of ±5% to the equilibrium constant values. It is on this basis that the equilibrium constant values in Table I have all been given to two significant figures.

The equation for the straight line of Figure 1 which has been found using the method of averages[7] is

$$\log K, \text{atm} = 8.06 \pm 0.27 - \frac{5200 \pm 150}{T}$$

The probable errors have been determined from the deviations of the experimental ordinate values from those calculated from the above equation.[7]

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(7) H. W. Salzberg, J. I. Morrow, S. R. Cohen, and M. E. Green, "Physical Chemistry, A Modern Laboratory Course," Academic Press, New York, N. Y., 1909, pp 6–40.

The resultant values for ΔS°_T and ΔH°_T, which are assigned to the mean temperature of our measurements, 550°K, are found to be $\Delta S^\circ_{550^\circ K} = 36.9 \pm 1.2$ gibbs mol^{-1}, $\Delta H^\circ_{550^\circ K} = 23{,}800 \pm 700$ cal mol^{-1}.

It is desirable that these values be corrected to the common standard temperature of 298°K. This can be done if the appropriate thermodynamic properties of the species involved are known, *i.e.* the heat capacities or the commonly quoted quantity, $H^\circ_T - H^\circ_{298}$. These data are available for CF_3OF and COF_2.[5] They have not been published for the peroxide, but spectroscopic studies of this species have been reported.[8,9] The authors of one of these studies[10] have computed the appropriate properties for this species from these data, and these are shown in Table II along with some interpolated values.

Table II. Thermodynamic Properties of CF_3OOCF_3

T, °K	S, gibbs mol^{-1}		$H^\circ_T - H^\circ_{298}$, cal mol^{-1}	
298.15	93.9[b]	95.7[c]	0.0	
400.0	104.1	106.0	3552.3[b]	3600.0[c]
493.0	112.4	114.5	7253	7360
550.0[a]	117.0	119.1	9737	9840
500[a]	113.0	115.3	7637	7640
600	121.2	122.9	11937	12040

[a] Interpolated graphically. [b] Data in this column based on the assumption that all frequencies are harmonic. [c] Data in this column based on assumption that CF_3 torsions are anharmonic.

For 550°K, from the data of Table II and published[5] data for CF_3OF and COF_2, it is found that $\Delta(H^\circ_{550} - H^\circ_{298}) = -667$ cal. The correction to ΔS° has been approximated $667/(550 - 298) \ln 550/298 = 1.6$ gibbs mol^{-1}. The resultant values at 298°K are $\Delta H^\circ_{298} = 24{,}500 \pm 700$ cal mol^{-1}, $\Delta S^\circ_{298} = 38.5 \pm 1.2$ gibbs mol^{-1}. These values may be combined with the heats of formation of the other species[5] at 298°K (CF_3OF, -184.0 ± 2.5 kcal mol^{-1}; COF_2, -151.7 ± 2 kcal mol^{-1}) and the standard entropies (CF_3OF, 73.6 gibbs mol^{-1}; COF_2, 61.9 gibbs mol^{-1}) to yield, for the peroxide, $\Delta H_f{}^\circ_{298} = -360.2 \pm 3.0$ kcal mol^{-1}, $S^\circ_{298} = 97.0 \pm 1.2$ gibbs mol^{-1}. It is of interest that the value for the standard entropy estimated using Benson's[11] structural contributions is 99.4 gibbs mol^{-1}, in good agreement with the value found here.

It is clear that use can be made of the thermodynamic quantities in Table II, for the peroxide, and recorded in the literature,[5] for the other species, to check the above results. The above entropy value, for example, can be compared with that shown in Table II, which is obtained completely independently. The present result is in good agreement with the spectroscopically determined entropy, especially with the value based on the assumption that the CF_3 torsional vibrations are anharmonic.

A further check on data of the present type, which is often made and is generally referred to as the third law analysis,[5] is to calculate ΔH°_{298} by the formula

$$\Delta H^\circ_{298} = -RT \ln K_p + T\Delta S^\circ_T - \Delta(H^\circ_T - H^\circ_{298})$$

In this expression, K_p is the experimental quantity and the other parameters are from the sources mentioned above. In this calculation of the enthalpy change, each point is independent of the others, and the method is capable of revealing erroneous trends in the data. Calculations made in this way for 500, 550, and 600°K yield values for ΔH°_{298} respectively of 24.8, 24.9, and 25.0 mol^{-1}. There is a trend in the data, but it is a very slight one. In addition, the agreement with the results reported above is excellent. The values reported above thus are considered reliable.

Discussion

It is of interest to compare the ΔH° for the present system with that for the hydrogen analog, dimethyl peroxide. The standard heat contents for dimethyl peroxide, methyl alcohol, and formaldehyde are respectively -30.0, -48.0, and -27.7 kcal mol^{-1},[11] which correspond to an exothermicity of 45.7 kcal mol^{-1}. The decomposition of bistrifluoromethyl peroxide, which is endothermic by 24.5 kcal mol^{-1}, thus represents a striking contrast to its hydrogen analog. A part of this is due to the difference between the strength of the O–F bond, 43.1 kcal mol^{-1}, and that of the O–H bond, 103 kcal mol^{-1},[11] and to the fact that the C–F bond is stronger than the C–H bond (*e.g.*, CH_3–F, $D_{298} = 108$ kcal mol^{-1}; CH_3–H, $D_{298} = 104$ kcal mol^{-1}).[11]

The consideration of the question of the strength of the oxygen–oxygen bond in bistrifluoromethyl peroxide makes it necessary to assign a value for the standard heat of formation of the trifluoromethoxy radical. Recently the activation energy of the first-order decomposition of trifluoromethyl hypofluorite has been reported[12] and interpreted in terms of the step

$$CF_3OF \longrightarrow CF_3O + F$$

If the assumption is made that the reverse step has zero activation energy,[13] then the activation energy for the forward step 43.5 ± 0.5 kcal mol^{-1} can be equated to the ΔH° of the reaction at the mean temperature of the experiments, *i.e.*, 493°K. This can be corrected to 298°K using the formula

$$\Delta H^\circ_{298} = \Delta H^\circ_{493} - \Delta C_{p,396}(195)$$

where $\Delta C_{p,396}$ is the difference between the sum of the product heat capacities and that of the reactant, at the mean temperature of 396°K. The pertinent values for CF_3OF and F have been taken from the literature,[5] while that for CF_3O has been approximated by subtracting from the value for CF_3OF a contribution for the O–F bond (approximated by the difference between the values for OF_2 and OF tabulated by Benson[11]). The correction is -350 cal mol^{-1}, so that the errors in estimating this correction are clearly negligible. The value used has therefore been 43.1 ± 0.5 kcal mol^{-1}. It thus follows that

$$\Delta H^\circ_{298}(CF_3O) = -184 \pm 2.5 - 18.9 + 43.1 = -159.8 + 2.5 \text{ kcal mol}^{-1}$$

The value of the bond strength in the peroxide, referred to 298°K, is thus

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[8] J. R. Durig and D. W. Wertz, *J. Mol. Spectrosc.*, **25**, 467 (1968).

[9] K. O. Christe, *Spectrochim. Acta, Part A*, **27**, 463 (1971).

[10] We are indebted to Professor Durig for kindly making these data available to us.

[11] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[12] J. Czarnowski, E. Castellano, and H. J. Schumacher, *Chem. Commun.*, 20, 1255 (1968).

[13] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

$$D_{CF_3O-OCF_3,298} = 360.2 \pm 3 - (319.6 \pm 3.5) = 40.6 \pm 5 \text{ kcal mol}^{-1}$$

This value may be compared to the corresponding values for dimethyl, diethyl, and di-*tert*-butyl peroxides, *i.e.*, 36.1 ± 1 ± 1, 34.1 ± 1, and 37.4 kcal mol^{-1}, respectively.[4] The bond in bistrifluoromethyl peroxide thus appears to be stronger than those in the dialkyl peroxides, although the difference is not outside of the error limits. A case for expecting a trend of this sort can be made using the arguments put forward to explain the high value for the oxygen-oxygen bond strength in dioxygen difluoride.[14-16] The answer to the question raised at the start of this article of the stability of CF_3OOCF_3 relative to dialkyl peroxides thus contains contributions from both factors mentioned there.

Although the study of a reaction equilibrium gives no direct information on the reaction paths involved, some comments can be made. The facts that[17] bistrifluoromethyl peroxide promotes the polymerization of hexafluoropropene at 275° and that the low molecular weight polymers had trifluoromethoxyl end groups constitute strong evidence that the initial step in the reaction involves cleavage of the oxygen-oxygen bond. In a recent study of the low-pressure pyrolysis of this compound,[18] carbon dioxide and carbonyl fluoride were observed as the main products, and the question as to whether the oxygen-oxygen bond of carbon-oxygen bond was the weaker was raised. In the present study, carbon dioxide is not a product and the equilibrium involves only the peroxide, trifluoromethyl hypofluorite, and carbonyl fluoride. These results are clearly most consistent with an oxygen-oxygen split. From a thermochemical point of view, it is possible to calculate the sum of the energy changes for the two-step process

$$CF_3OOCF_3 \longrightarrow CF_3OO + CF_3$$

$$CF_3OO \longrightarrow CF_3 + O_2$$

from the heats of formation of the peroxide and of the trifluoromethyl radical, which is −115.7 ± 2.0 kcal mol^{-1}.[5] This yields a value of 128.8 ± 4 kcal mol^{-1}. The allocation of the contributions of the individual carbon-oxygen bonds is not straightforward, but it may be pointed out that the corresponding values can be calculated from available thermodynamic data for hydrogen peroxide and estimated for dimethyl peroxide.[11] In each case, cleavage of the first bond to oxygen requires considerably more energy than does cleavage of the bond to oxygen in the R-OO radical. (The strength of the first carbon-oxygen bond in dimethyl peroxide is calculated as 71 kcal mol^{-1}, a value considerably below that usually cited[11] for the C-O bond dissociation energy, *i.e.*, 81.5 kcal mol^{-1}.) Cleavage of bistrifluoromethyl peroxide at the carbon-oxygen bond would be expected to require in excess of 65 kcal mol^{-1}, and on this basis the oxygen-oxygen cleavage is favored.

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(15) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).

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Iodine-Sensitized Photoformation of Singlet Oxygen

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Contribution from the Chemistry Department, American University of Beirut, Beirut, Lebanon. *Received July 29, 1971*

Abstract: The use of iodine as a triplet sensitizer for production of singlet oxygen in hydrocarbon solution at room temperature has been investigated. The production of singlet oxygen was inferred from disappearance of an organic substrate, naphthacene or 1,3-diphenylisobenzofuran (DPIBF), upon irradiation. Direct excitation of I_2 molecules to the $^3\Pi_u$ state leads to the appearance of singlet oxygen, but the energy transfer reaction $^3I_2 + {}^3O_2 \rightarrow I_2 + {}^1O_2$ is some five orders of magnitude less efficient than the similar reaction involving naphthacene, $^3I_2 + \text{Nc} \rightarrow I_2 + {}^3\text{Nc}$. Other results of the studies are that naphthacene is two orders of magnitude less reactive with singlet oxygen than is DPIBF, and in the iodine-DPIBF system, all photooxidation is caused by iodine to oxygen direct energy transfer, whereas in the iodine-naphthacene system, nearly all singlet oxygen is generated by a two stage, iodine-naphthacene-oxygen energy transfer chain.

The detailed mechanisms of organic photooxidation processes have, in recent years, been the subject of several comprehensive investigations,[1,2] which have demonstrated that the triplet state of the absorbing organic species (sensitizer) is part of the energy transfer path and that this triplet state undergoes an energy transfer reaction with ground state oxygen molecules to produce excited singlet oxygen molecules which then add to the substrate to form the oxidation product(s). Although both autooxidations (sensitizer and oxidant identical) and sensitized oxidations (sensitizer and oxidant different) have been examined, in all cases reported to date the sensitizer has itself been an organic light absorber.

In principle, triplet state molecules other than those of an organic nature can also serve as sensitizers for

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