# Bis(perfluoroalkyl) Trioxides[1]

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**Abstract:** The isolation, identification, and characterization of the novel class of compounds, the bis(perfluoroalkyl) trioxides, are described. Bis(perfluoromethyl) trioxide and perfluoromethyl perfluoroethyl trioxide are discussed. Bis(perfluoroalkyl) trioxides possess surprising thermal stability. $CF_3OOOCF_3$ slowly decomposes to $CF_3OOCF_3$ and $O_2$ with a half-life of approximately 65 weeks at 25°.

There has been considerable discussion in the past few years concerning the existence, stability, and isolation of polyoxides of hydrogen as well as alkyl polyoxides.[2] However, reports of the existence of such compounds have remained questionable. For example, Dasent[3] states that no compound is known in which more than two oxygen atoms are joined together by a single bond. Compounds containing multiple bonding such as ozone and ozonide ions are, of course, well known. Multiple bonding is also involved in the series of oxygen fluorides, $O_2F_2$ through $O_6F_2$.[4]

Recently, Milas and Arzoumanidis claimed to have isolated di-*t*-butyl trioxide,[5] but Bartlett and Günther[6] demonstrated that the above compound was actually 2,2-di-*t*-butylperoxypropane. In addition, the latter authors reported that the low-temperature oxidation of *t*-butyl and cumyl hydroperoxides apparently proceeded *via* the formation of trioxide intermediates, which were only stable at low temperature.[6]

It is of interest, therefore, to report the preparation, isolation, and characterization of two members of the new class of compounds, the bis(perfluoroalkyl) trioxides. Examples presented in this paper are $CF_3OOOCF_3$[7,8] and $CF_3OOOC_2F_5$.

## Results and Discussion

Bis(perfluoroalkyl) trioxides are obtained in moderately low yield by the direct fluorination of salts of trifluoroacetic acid.[9,10] Various salts have been used, including sodium, potassium, magnesium, calcium, and aluminum trifluoroacetates. Fluorinations of these salts also give many other volatile products in varying amounts and are the subjects of other papers.[10,11] The predominant products are usually $C_2F_5OF$ and $CF_3CF(OF)_2$. Other products include $CF_2(OF)_2$, $CF_3OF$, $CF_3OCF_3$, $CF_3OC_2F_5$, $CF_3OOCF_3$, $CF_3OOC_2F_5$, $C_2F_5OOC_2F_5$, $CF_3OOF$, and $C_2F_5OOF$. The synthetic route using $OF_2$ with $COF_2$ employed by Anderson and Fox[7] is a far superior method for the preparation of $CF_3OOOCF_3$ and may also be a general reaction for the synthesis of trioxides. The structures of $CF_3OOOCF_3$ and $CF_3OOOC_2F_5$ have been assigned on the basis of $^{19}F$ nmr spectra, elemental analyses, and molecular weights, and are supported by infrared and mass spectra.

**Bis(perfluoromethyl) Trioxide ($CF_3OOOCF_3$).** Isolation and purification of $CF_3OOOCF_3$ were performed using fractional distillation–condensation on a vacuum line followed by gas chromatography. It is a colorless gas with an estimated boiling point between −10 and −20°.

In Table I the $^{19}F$ nmr spectrum of bis(perfluoromethyl) trioxide is compared with the nmr spectra of the corresponding ether and peroxide. The similarity in shielding of the trioxide and peroxide compared to the marked decrease in shielding for the ether when both $CF_3$ groups are attached to the same oxygen atom is analogous to the effect Tiers of our laboratories has reported for fluorocarbon sulfides, disulfides, and trisulfides.[12] Since a value for the F–F′ coupling constant cannot be determined for a symmetrical molecule such as bis(perfluoromethyl) trioxide, except *via* the very weak $^{13}C$ satellites, the nmr spectrum of $CF_3OOOCF_3$ demonstrates only that there is but one type of fluorine atom in the molecule and that this type is in an environment very similar to that of bis(perfluoromethyl) peroxide.

**Table I.** $^{19}F$ Nmr Spectral Data

| Compd | $\phi$* | Multiplicity |
|---|---|---|
| $CF_3OOOCF_3$ | 68.7 | Singlet |
| $CF_3OOCF_3$ | 69.0 | Singlet |
| $CF_3OCF_3$ | 58.3 | Singlet |

The elemental analyses and molecular weight determined for this compound (see Experimental Section) establish that its formula is $C_2F_6O_3$. These data, together with the nmr spectrum, establish the structure as $CF_3OOOCF_3$.

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(1) This research was supported by the Advanced Research Projects Agency under Contract NOrd 18688 and was monitored by the Bureau of Naval Weapons.

(2) S. W. Benson, *J. Chem. Phys.*, **33**, 306 (1960); S. W. Benson, *J. Am. Chem. Soc.*, **86**, 3922 (1964), together with references cited therein.

(3) W. E. Dasent, "Nonexistent Compounds," Edward Arnold (Publishers) Ltd., London, 1965, pp 55–56.

(4) A. G. Streng and A. V. Grosse, *J. Am. Chem. Soc.*, **88**, 169 (1966); R. D. Spratley and G. C. Pimentel, *ibid.*, **88**, 2395 (1966); A. D. Kirshenbaum and A. G. Streng, *ibid.*, **88**, 2434 (1966), together with references cited therein.

(5) N. A. Milas and G. G. Arzoumanidis, *Chem. Ind.* (London), 66 (1966).

(6) P. D. Bartlett and P. Günther, *J. Am. Chem. Soc.*, **88**, 3288 (1966).

(7) Subsequent to this work, L. R. Anderson and W. B. Fox discovered an elegant synthesis of $CF_3OOOCF_3$ [*ibid.*, **89**, 4313 (1967)].

(8) Also subsequent to this work, the photolysis of perfluoroazomethane and oxygen was reported to yield a compound, $CF_3O_3CF_3$, but insufficient data were given to allow comparison with $CF_3OOOCF_3$: V. A. Ginsburg, *et al.*, *Dokl. Akad. Nauk SSSR*, **149**, 97 (1963).

(9) P. G. Thompson, "Oxygen Fluorides and Hypofluorites," the Fluorine Symposium of the Inorganic Division of the American Chemical Society, Ann Arbor, Mich., June 27, 1966.

(10) P. G. Thompson, to be published.

(11) P. G. Thompson, *J. Am. Chem. Soc.*, **89**, 1811 (1967).

(12) G. V. D. Tiers, *J. Phys. Chem.*, **66**, 764 (1962).

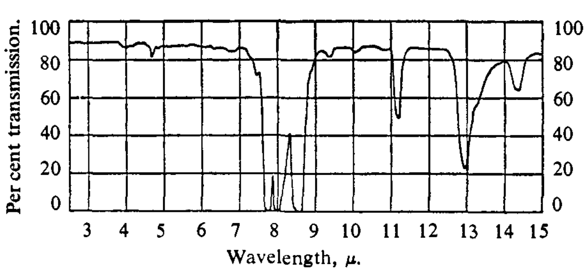

Figure 1. Infrared spectrum of $CF_3OOOCF_3$: 40 mm pressure, 25-mm cell.

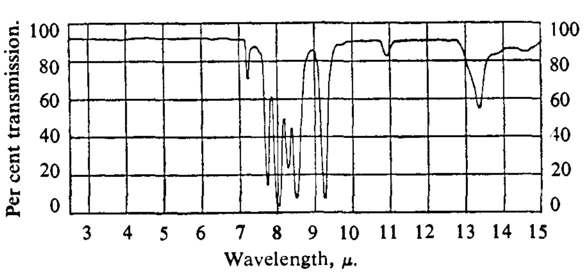

Figure 2. Infrared spectrum of $CF_3OOOC_2F_5$: 12 mm pressure, 25-mm cell.

The infrared spectrum of bis(perfluoromethyl) trioxide is shown in Figure 1. The spectrum has strong bands in the C–F stretching region at 7.74, 7.99, and 8.56, moderate absorption at 11.16 and 12.94 (weak shoulder at 13.28), a weak band at 14.36, and very weak absorption at 4.72, 9.38, and 10.07 μ. The spectrum of $CF_3OOOCF_3$ has a resemblance to the spectra of $CF_3OOCF_3$[13] and $CF_3OCF_3$,[14] particularly in the C–F stretching region.

The mass spectrum of $CF_3OOOCF_3$, as shown in Table II, is consistent with the assigned structure. The mass spectra of $CF_3OOOCF_3$, $CF_3OOCF_3$, and $CF_3OCF_3$ show many similarities. All three spectra have $m/e$ 69 ($CF_3^+$) as the base peak. All three also show $m/e$ 47 ($CFO^+$) as the second largest peak; its relative intensity, however, decreases considerably from trioxide to peroxide to ether as the relative amount of oxygen in the compound decreases. This decrease also occurs for other oxygen-containing fragments. An increase in relative intensity is observed for the higher mass ions, such as the molecular ion (parent) or $(P - F)^+$, when comparing spectra of the trioxide to peroxide to ether.

**Table II.** Mass Spectrum of $CF_3OOOCF_3$

| $m/e$ | Ion | Rel intensity | $m/e$ | Ion | Rel intensity |
|---|---|---|---|---|---|
| 16 | $O^+$ | 1.1 | 47 | $CFO^+$ | 33.2 |
| 19 | $F^+$ | 1.7 | 50 | $CF_2^+$ | 4.9 |
| 28 | $CO^+$ | 8.7 | 66 | $CF_2O^+$ | 12.7 |
| 31 | $CF^+$ | 5.2 | 69 | $CF_3^+$ | 100.0 |
| 32 | $O_2^+$ | 2.2 | 82 | $CF_2O_2^+$ | 1.0 |
| 44 | $CO_2^+$ | 4.2 | | | |

The ultraviolet spectrum of $CF_3OOOCF_3$ showed no absorption between 400 and 260 mμ and only negligible end absorption beginning at 260 to 220 mμ (ε 0.3 at 220 mμ).

**Perfluoromethyl Perfluoroethyl Trioxide ($CF_3OOOCF_2CF_3$).** Fractionation by standard vacuum line techniques followed by gas chromatography were also used to separate and purify $CF_3OOOC_2F_5$. It is a colorless gas with an estimated boiling point between 10 and 20°. Elemental analyses and molecular weight data for this compound (see Experimental Section) establish its molecular formula as $C_3F_8O_3$.

The $^{19}F$ nmr spectrum of $CF_3OOOC_2F_5$ is even more useful in establishing the structure than in the case of $CF_3OOOCF_3$ since the perfluoroalkyl groups are different. Nmr spectral data for perfluoromethyl perfluoroethyl trioxide are compared in Table III with data of the corresponding ether and peroxide. Note that the nmr spectrum of the methyl ethyl trioxide bears the same close resemblance to the corresponding peroxide as the dimethyl trioxide has to the dimethyl peroxide. There are very minor shifts in the spectral position, but the main distinction is that, whereas the $CF_3$ group is split by the $CF_2$ group across the two intervening oxygen atoms in $CF_3OOCF_2CF_3$, no coupling is observed across the three intervening oxygen atoms. This case is also analogous to that reported by Tiers[12] concerning the polysulfides mentioned above.

The $^{19}F$ nmr spectra of several dozen ethers, peroxides, and trioxides are tabulated (Table IV) and the chemical shifts are found to give extremely good correlation for the group involved. There is close similarity in shielding for peroxides and trioxides compared to that for ethers which have a marked decrease in shielding for α fluorines and an increase in shielding for β fluorines. Furthermore, distinguishing between unsymmetrical ethers, peroxides, and trioxides, such as $CF_3O_{1-3}C_2F_5$, is readily done by examining the appropriate F–F′ coupling constants. The coupling constants for ethers are 9–10 cps; for peroxides, 4–5 cps; and for trioxides (or higher multioxygen linkages) <1 cps. For trioxides, $J$ is probably a very small number, say 0.3 cps, and even smaller for tetroxides. The method just described for determining the number of oxygens between perfluoroalkyl groups is much easier than attempting to analyze splitting patterns of the weak $^{13}C$ satellites.

Thus, the conclusive analysis of the $^{19}F$ nmr spectrum together with the elemental analyses and molecular weight data for this compound unambiguously establish its structure as $CF_3OOOCF_2CF_3$.

The infrared spectrum of perfluoromethyl perfluoroethyl trioxide (Figure 2) has a striking resemblance to the spectra of perfluoromethyl perfluoroethyl ether and perfluoromethyl perfluoroethyl peroxide, which were also obtained as minor products in this work.[15]

The mass spectrum of $CF_3OOOCF_2CF_3$ (Table V) is also consistent with the assigned structure. The spectra of $CF_3OOOC_2F_5$, $CF_3OOC_2F_5$, and $CF_3OC_2F_5$ not only have many similarities among the three, but also

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(13) The infrared spectrum of $CF_3OOCF_3$ shows absorptions at 7.80 (s), 7.94 (s), 8.09 (m), 8.60 (s), and 8.92 μ (w). See also R. S. Porter and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 5628 (1957); A. J. Arvia and P. J. Aymonino, *Spectrochim. Acta*, **18**, 1299 (1962).

(14) D. G. Weiblen in "Fluorine Chemistry," Vol. II, J. H. Simons, Ed., Academic Press Inc., New York, N. Y., 1954, p 479.

(15) Absorptions are found: (a) for $CF_3OOOC_2F_5$ at 7.24 (w), 7.74 (s), 8.03 (vs), 8.28 (s), 8.49 (s), 9.24 (s), 10.92 (w), and 13.36 μ (m): (b) for $CF_3OOC_2F_5$ at 7.25 (w), 7.74 (s), 8.02 (s), 8.27 (m), 8.54 (s), and 9.22 μ (s): and (c) for $CF_3OC_2F_5$ at 7.10 (w), 7.78 (s), 8.01 (s), 8.46 (shoulder), 8.64 (s), 9.04 (m), 9.74 (w), 11.07 (m), 12.05 (w), 13.25 (m), and 14.72 μ (m). Relative intensities are given by the usual symbols in parentheses.

Table III. $^{19}$F Nmr Spectral Data

| | | | |
|---|---|---|---|
| Cps | <1   1.5 | 4.3   1.5 | 9.2   ~2.2 |
| | $CF_3—O—O—O—CF_2—CF_3$ | $CF_3—O—O—CF_2—CF_3$ | $CF_3—O—CF_2—CF_3$ |
| | (s) (q) (t) | (t) (q,q) (t) | (t) (q,q) (t) |
| $\phi^*$ | 68.7 96.4 83.8 | 68.7 95.7 83.2 | 56.2 91.2 87.6 |

Table IV. Structure Determination of $R_fO_{1-3}R_f'$ by $^{19}$F Nmr

| | $\mathit{CF_3}$O-[a] | $CF_3$-<br>$\mathit{CF_2}$O-[a] | $\mathit{CF_3}$-<br>$CF_2$O-[a] | $J$[b]<br>$-CF_2O_nCF_2-$ |
|---|---|---|---|---|
| Ethers | 55–58 | 87–88 | 88–91 | 9–10 |
| Peroxides | 68–69 | 83–84 | 96–98 | ~4 |
| Trioxides | 68–69 | 83–84 | 96–98 | <1 |

[a] $\phi^*$. [b] In cycles per second.

with the spectra of the corresponding $CF_3O_{1-3}CF_3$ compounds discussed above. In general, the same comments apply; however, the spectrum of $CF_3OC_2F_5$ differs from the spectra of $CF_3OOC_2F_5$ and $CF_3OOOC_2F_5$ considerably more than in the previous series. For example, its four largest peaks are at *m/e* 69, 119, 31, and 50. This is, of course, not too surprising considering the small proportion of oxygen in $CF_3OC_2F_5$.

Table V. Mass Spectrum of $CF_3OOOCF_2CF_3$

| *m/e* | Ion | Relative intensity | *m/e* | Ion | Relative intensity |
|---|---|---|---|---|---|
| 16 | $O^+$ | 5.2 | 50 | $CF_2^+$ | 26.9 |
| 19 | $F^+$ | 5.5 | 66 | $CF_2O^+$ | 33.9 |
| 28 | $CO^+$ | 24.3 | 69 | $CF_3^+$ | 100.0 |
| 31 | $CF^+$ | 22.7 | 82 | $CF_2O_2^+$ | 1.8 |
| 32 | $O_2^+$ | 1.4 | 85 | $CF_3O^+$ | 1.6 |
| 44 | $CO_2^+$ | 15.4 | 97 | $C_2F_3O^+$ | 2.3 |
| 47 | $CFO^+$ | 87.8 | 119 | $C_2F_5^+$ | 17.5 |

**Properties of Trioxides.** Perfluoroalkyl trioxides[16] are interesting compounds to compare with oxygen fluorides such as $O_2F_2$ and $O_3F_2$. The structure of $O_2F_2$ is somewhat analogous to that of $H_2O_2$, but with a greatly shortened O–O bond distance and exceptionally long O–F bonds.[17] The structure and bonding in $O_3F_2$, however, have not yet been determined in spite of much effort.

Since a perfluoromethyl radical has a certain pseudohalogen character and an electronegativity between that of fluorine and chlorine,[18] one might consider bis(perfluoromethyl) trioxide to be a higher homolog of $O_3F_2$. However, the bis(perfluoroalkyl) trioxides possess surprising thermal stability, in marked contrast to $O_3F_2$ or even to $O_2F_2$, which decompose readily above $-160$ or $-100°$, respectively.[19]

A sample of $CF_3OOOCF_3$, sealed in a Pyrex nmr tube together with $CFCl_3$ as an internal reference, had undergone approximately a 25% decomposition to $CF_3OOCF_3$ after 25 weeks and approximately a 40% decomposition after 47 weeks at 25°. Analysis of the products showed that thermal decomposition at 25° occurred primarily[20] by the following reaction.

$$CF_3OOOCF_3 \xrightarrow{\Delta} CF_3OOCF_3 + 0.5O_2$$

The half-life for this reaction was found to be approximately 65 weeks at 25°. This half-life for $CF_3OOOCF_3$ at room temperature is remarkable when one considers that $O_3F_2$ has a half-life of only 9 hr at $-160°$. Using the experimentally determined value of 65 weeks for the half-life of the above reaction, the bond dissociation energy, $D(CF_3O\text{–}OOCF_3)$, was calculated to be 29–30 kcal/mole.[21]

Perfluoroalkyl trioxides are oxidizing agents, *e.g.*, oxidizing solutions of potassium iodide or ferrocene.

## Experimental Section

Fluorination procedures, isolation, purification, analysis, and characterization of these compounds were similar to procedures described in other papers.[10,11,22] Gas chromatography columns used were packed with perfluorotributylamine[23] coated on 30–60 mesh acid-washed Celite.[24] For preparative-scale separations a 0.5-in. diameter column 8 ft, 7 in. in length was used with dry helium flow rates of 150–320 cc/min. For analytical work with $CF_3OOOCF_3$ a 0.25-in. diameter column 24 ft in length was used with a flow rate of 75 cc min.

Infrared spectra were obtained on a Perkin-Elmer Model 21 double-beam instrument using a 25-mm gas cell equipped with NaCl windows. Ultraviolet spectra were obtained on a Cary Model 11 instrument using 10-cm gas cells equipped with $CaF_2$ windows. Mass spectra were obtained using a Consolidated 21-103C instrument with an inlet temperature of 30°, ion chamber temperature of 250°, ionizing voltage of 70 v, and ion current of 10 $\mu$a. Fluorine nmr spectra were measured with a Varian V-4300-2 instrument operating at 40.0 Mc. Shielding values are reported in $\phi^*$[25] units at concentrations of about 15–30 mole % sample in $CFCl_3$ as solvent and internal reference, negative values for low field. All precision measurements (chemical shifts and coupling constants of spin–spin splittings) were made according to techniques described by Tiers.[26] Side bands were produced by amplitude modulation of the radiofrequency[27] for reasons discussed previously.[28] It should be noted that measurements made on pure liquids using an external reference cannot accurately be converted to $\phi$ values. Even if the sample is in solution, the posi-

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(16) Although the only trioxides to be isolated and unambiguously identified have been $CF_3OOOCF_3$ and $CF_3OOOC_2F_5$, $C_2F_5OOOC_2F_5$ was also formed in very small yield as determined by $^{19}$F nmr (absorption at approximately $\phi$ 83 and 95 in correct area ratios) and glpc retention times (eluting after several similar compounds having a molecular weight of 236 and shortly before another component having a molecular weight of 286). Still another component had a single sharp peak at $\phi$ 69 in its nmr spectrum and may possibly have been the tetroxide, $CF_3OOOOCF_3$. However, the compound was present in too low a concentration together with another component and could not be isolated for identification.

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

(18) J. J. Lagowski, *Quart. Rev.* (London), **13**, 233 (1959).

(19) A. G. Streng, *Chem. Rev.*, **63**, 607 (1963).

(20) Small amounts of $SiF_4$ and $CO_2$ as well as trace amounts of $CF_2Cl_2$ (from the $CFCl_3$) were also found. It is assumed that heating $CF_3OOOCF_3$ in glass would result in the reaction $CF_3OOOCF_3 + 1.5SiO_2 \rightarrow 1.5SiF_4 + 2CO_2 + O_2$.

(21) It was assumed that (1) the dissociation of an O–O bond was first order and the rate-determining step in the thermal decomposition of $CF_3OOOCF_3$, (2) the activation energy was zero,[2] and (3) the Arrhenius *A* factor = $10^{13.5}$ sec$^{-1}$. This value was kindly provided by Dr. A. S. Rodgers, formerly of these laboratories, who is now a member of Dr. Benson's group at Stanford Research Institute.

(22) P. G. Thompson and J. H. Prager, *J. Am. Chem. Soc.*, **89**, 2263 (1967).

(23) FC-43 (3M Co.).

(24) Chromosorb P (Johns-Manville).

(25) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(26) G. V. D. Tiers, *ibid.*, **62**, 1151 (1958).

(27) G. V. D. Tiers, *ibid.*, **67**, 928 (1963).

(28) J. H. Prager and P. G. Thompson, *J. Am. Chem. Soc.*, **87**, 230 (1965).

tion of an external reference is appreciably different than if the reference is internal. It is for these reasons as well as those discussed by Tiers that $^{19}F$ nmr data should be reported in a truly interconvertible system of units such as $\phi$ values.

**Safety Precautions.** Although no explosions of bis(perfluoroalkyl) trioxides have been observed during the course of this work, the same safety precautions previously described[22] for fluoroxy compounds have been observed.

**Fluorination of Sodium Trifluoroacetate.** A 2.1-g (15.6 mmoles) sample of finely divided dry sodium trifluoroacetate in a monel sintered-plate reactor was treated with 0.30 mole of fluorine under the following conditions: 4% $F_2$, 15 min; 20% $F_2$, 1 hr; 34% $F_2$, 2 hr. The temperature of the reactor gradually increased from 17 to 22°. The volatile products condensed in the liquid oxygen trap (9.3 mmoles) were analyzed by gas chromatography after work-up by standard vacuum line procedures. Approximately 4% of $CF_3OOOCF_3$ was found together with smaller amounts of $CF_3OOOC_2F_5$. Yields of $CF_3OOOCF_3$ were generally 1–5%.

**Bis(perfluoromethyl) Trioxide.** Bis(perfluoromethyl) trioxide was purified by gas chromatography at $-30°$. Its retention time was found to be approximately 60 relative to fluorotrichloromethane. Elemental analyses were obtained on a sample of chromatographed $CF_3OOOCF_3$. A molecular weight determination on this material gave a value of 187 (calcd, 186).

*Anal.* Calcd for $C_2F_6O_3$: C, 12.9; F, 61.3. Found: C, 13.0; F, 60.4.

**Perfluoromethyl Perfluoroethyl Trioxide.** Perfluoromethyl perfluoroethyl trioxide was purified by gas chromatography at 0°. Its retention time was found to be approximately 150 relative to fluorotrichloromethane. Elemental analyses were obtained on a sample of chromatographed $CF_3OOOC_2F_5$. Unfortunately the sample was then contaminated by a small amount of $CFCl_3$. A quantitative measurement of the amount of $CFCl_3$ in the sample was made by both infrared and mass spectroscopy. The two determinations were in good agreement and the calculated values for $C_3F_8O_3$ are adjusted for the 4 wt % $CFCl_3$ present. A molecular weight determination on this sample gave a value of 234; calcd (cor), 232.

*Anal.* Calcd for $C_3F_8O_3$ (cor): C, 15.0; F, 62.4. Found: C, 15.0; F, 62.0.

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# Kinetics of Ligand Exchange by Nuclear Magnetic Resonance Complete Line-Shape Techniques. I. Exchange of 2-Picoline with Dichlorobis(2-picoline)cobalt(II)

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*Contribution from the William A. Noyes Laboratory, University of Illinois, Urbana, Illinois.* *Received February 20, 1967*

**Abstract:** The exchange kinetics of excess 2-picoline with dichlorobis(2-picoline)cobalt(II) in acetone-$d_6$ were investigated by nuclear magnetic resonance computerized, complete line-shape techniques. Exchange rates were measured between $-39$ and $-60°$, and in this region it was found that $1/\tau_M = K_2[\text{2-picoline}]$. The Arrhenius activation energy for $K_2$ is $E_a = 5.3 \pm 0.3$ kcal/mole.

In recent years many studies have been conducted on the exchange kinetics of inorganic complexes *via* nuclear magnetic resonance.[2,3] Most of these studies have involved octahedral complexes in aqueous solution or in the free ligand as solvent.[4-9] Thus, there was no opportunity to definitively study, in a relatively inert solvent, the role of the free ligand in the exchange mechanism. Also, these studies have almost exclusively employed line-broadening methods to obtain the exchange rates.

Very little is known about the exchange kinetics of tetrahedral complexes. When this study was begun, no nmr exchange studies had been conducted on this type of system.[10] Thus, it was of interest to us to study the exchange reactions of tetrahedral complexes in a relatively inert solvent where the concentration of free ligand could be varied. An additional purpose of this work was to test the feasibility of using computerized, complete line-shape techniques to evaluate the exchange rates for paramagnetic systems where the signals are broad and the signal-to-noise ratio is usually not favorable due to limited complex solubility. Application of the line-shape method is desirable, since it appears to be inherently more accurate than line-broadening techniques.[11] Also, the former method is more versatile, since it is applicable over the entire temperature range in which the exchange rate influences the signal shape.

With these goals in mind we chose $Co(2\text{-pic})_2Cl_2$, which has been previously characterized,[12,13] for ex-

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(1) Abstracted in part from the Ph.D. thesis of S. Zumdahl, University of Illinois, Urbana, Ill.; University of Illinois Fellow, 1964–1966; Toni Co. Fellow, 1966–1967.

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(12) D. P. Graddon and E. C. Watton, *Australian J. Chem.*, **18**, 507 (1965).