Table I. Rate Constants and Activation Energies for Hindered Internal Rotation of *N,N*-Dimethyltrichloroacetamide as Determined by Proton and Carbon Magnetic Resonance

Field strength, MHz, nucleus	Method	Solvent	E_a, kcal/mol	T_c,[b] °C	$\Delta F^{\ne}(T_c)$,[c] kcal/mol	$k(T_c)$, sec^{-1}
60, proton	Ss[a]	30% DFTE[f]	16.4 ± 0.8	13	17.5	0.027
90, proton	Ss	30% DFTE	17.4 ± 0.8	~21	18.3	0.0168
22.6, carbon	Ss	30% DFTE	16.6 ± 0.8	15	17.6	0.0268
26.9, proton	Se	Neat	14.6 ± 0.6	~18.5	18.0[d]	0.0167[e]

[a] Ss = signal-shape analysis. Se = spin echo. [b] T_c = coalescence temperature. [c] $\Delta F^{\ne}$ = free energy calculated at coalescence temperature. [d] Calculated using rate constant at 17° obtained from spin-echo measurements; ref 4. [e] Rate constant at 17° from spin-echo measurements; ref 4. [f] DFTE is 1,2-dibromotetrafluoroethane.

MHz pmr spectra were observed on a Varian A-56/60 spectrometer with a calibrated "standard" methanol sample used to determine temperature. The DMTCA was prepared and purified according to Brintzinger's method.[8]

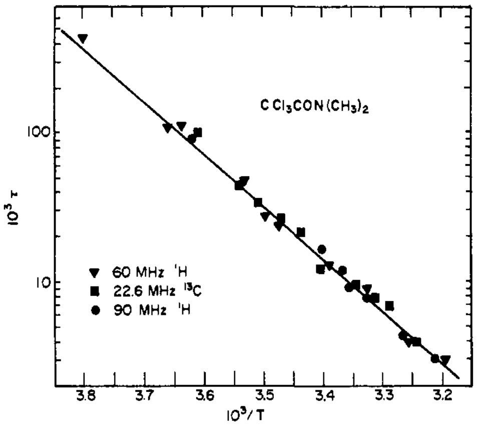

Figure 2. Arrhenius activation energy plot for hindered internal rotation of *N,N*-dimethyltrichloroacetamide. The τ values are relaxation times measured from computer-fitted 60-, 90-, and 22.6-MHz spectra.

Proton and carbon spectra were obtained throughout the temperature range -10 to $+50°$. Several actual and computer-simulated cmr spectra from which reported relaxation times (τ) were determined are presented for comparison purposes in Figure 1. Rate constants, $k = 1/2\tau$, and activation energies listed in Table I were calculated using multiple linear regression analysis program No. 1971A on a Wang 700 programming calculator.

Free energies of activation, ΔF, were obtained from exchange rates at pmr, cmr coalescence temperatures and compare quite well with those measured from spin-echo nmr by Allerhand and Gutowsky. Agreement among pmr and cmr activation energies measured in this work is excellent and is within 10% of the spin-echo value measured for neat DMTCA. Figure 2 is an Arrhenius plot of all data measured at 60, 90, and 22.6 MHz, which firmly establishes the validity of cmr as a method for kinetic studies.

Several experimental caveats are necessary. First, spectra reported are presently the absolute limit of cmr sensitivity. Several thousand repetitive pulses were necessary. We anticipate the need to use ~10% ^{13}C-enriched materials for other measurements. Secondly, as lines broaden or as measurements are performed at higher temperatures on, for example, *N,N*-dimethylformamide (DMF), sensitivity drops dramatically for two reasons: (a) Boltzman populations readjust, (b) large, low-temperature shift differences between the two methyls of DMF (5.3 ppm) cause broadening and coalescening over a large spectral area. Large shift differences make data collection more difficult, but the wider temperature range over which cmr data may be obtained will provide activation energies more accurate than those obtained by pmr methods.

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Crystal Structure of Potassium Tris(oxalato)rhodate(III)

Sir:

We have undertaken the determination of the structure of $K_3[Rh(C_2O_4)_3]\cdot 4.5H_2O$ in order to establish whether all oxalato groups are bis chelated or, as some earlier studies seemed to indicate, the complex should be written as $K_6[Rh(C_2O_4)_3][Rh(C_2O_4)_2(C_2O_4H)(OH)]\cdot 8H_2O$. The latter formulation denotes that one oxalato group per two Rh(III) centers is singly bonded to rhodium, the remaining coordination site being occupied by a hydroxyl group or by a water molecule. This formulation was suggested (a) by a study of the solid-state broad-line proton magnetic resonance spectrum,[1] in which certain peaks, at temperatures varying from -196 to 45°, were assigned to protons in waters (or hydroxyls) directly coordinated to the rhodium center; (b) by dehydration data;[1] and (c) by consideration of the kinetics of the oxalate exchange and aquation reactions of the complex in solution, in which a monoaquated tris(oxalato)rhodate(III) ion was postulated to preexist.[2] More recent support for a dangling oxalate in the solid was cited by Gillard, *et al.*,[3] who interpret their dta curves at 200° in terms of the removal of one-half of a constitutional water molecule per Rh.

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(8) H. Brintzinger, K. Pfannsteil, and H. Koddebusch, *Chem. Ber.*, **82**, 399 (1949).

(1) A. L. Porte, H. S. Gutowsky, and G. M. Harris, *J. Chem. Phys.*, **34**, 66 (1961).

(2) D. Barton and G. M. Harris, *Inorg. Chem.*, **1**, 251 (1962).

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The potassium salt of the complex was recrystallized from aqueous solution as the orange 4.5-water compound.[4] The unit cell is triclinic, with $a = 6.825$, $b = 10.457$, $c = 12.428$ Å, $\alpha = 103.70°$, $\beta = 96.17°$, $\gamma = 85.40°$, and $V = 855.4$ Å^3, and contains two formula units of the monomeric compound. The calculated density is 2.195 g/ml, compared to a value of 2.152 g/ml determined by flotation in mixtures of $CHBr_3$ and CCl_4. The space group is $P\bar{1}$. Precession film data were taken using crystals oriented around the crystallographic c and b axes, respectively. Intensities were estimated visually by comparison with a calibrated standard, corrected for geometrical factors, and brought to a common scale. No absorption correction was applied in view of the small dimensions of the crystals. A total of 1245 independent, observed reflections were thus obtained and used in the structure determination.[5] Preliminary positional parameters for most atoms could be determined from a three-dimensional Patterson map. The remaining atoms were located from a computed electron density map, and the positions of all atoms were refined using least-squares and Fourier methods. The water molecule which corresponds to the 0.5 H_2O in the stoichiometric formula of the compound was found to be disordered and situated close to a center of inversion, far removed from the complex ion, so that it definitely is not coordinated to the Rh(III) center. The final least-squares refinement, which included anisotropic thermal parameters for each atom, resulted in a residual R of 0.076. The resultant electron density map was featureless, with the exception of some small ripple in the immediate environment of the rhodium atom. In order to establish the centrosymmetric structure beyond question, several series of refinements were carried out in which successively each of the oxalato rings of one Rh complex was opened at one end and the symmetry was reduced to $P1$. The models thus obtained were carried through one or more refinement cycles, but in every instance the model either refined back to the centrosymmetric structure or the refinements did not converge at all. These calculations proved not only that the center of symmetry exists, but also that no dangling oxalato groups occur in the structure of the complex. The atomic coordinates and their standard deviations are shown in Table I.

Table I. Fractional Atomic Coordinates from the Final Anisotropic Refinement[a]

Atom	X	Y	Z
Rh	0.16146 (32)	0.18833 (12)	0.29960 (10)
K(1)	0.44503 (101)	−0.12975 (41)	0.09772 (30)
K(2)	−0.25096 (101)	0.24585 (36)	0.45012 (31)
K(3)	0.29977 (106)	0.32686 (41)	0.67464 (32)
O(1)	−0.09910 (235)	0.10105 (113)	0.24792 (87)
O(2)	0.16109 (255)	0.19028 (122)	0.13903 (92)
O(3)	0.01193 (200)	0.36558 (118)	0.32446 (112)
O(4)	0.40447 (256)	0.29811 (120)	0.34490 (97)
O(5)	0.16076 (251)	0.17488 (101)	0.45753 (83)
O(6)	0.31071 (250)	0.01128 (106)	0.28752 (93)
O(7)	−0.31034 (353)	0.07169 (133)	0.10111 (105)
O(8)	−0.04309 (277)	0.15936 (138)	−0.01593 (88)
O(9)	0.08059 (357)	0.57629 (104)	0.37172 (127)
O(10)	0.47941 (381)	0.50198 (148)	0.38005 (137)
O(11)	0.21407 (311)	0.02959 (119)	0.56099 (94)
O(12)	0.36650 (391)	−0.14682 (123)	0.38038 (122)
C(1)	−0.15053 (364)	0.10454 (151)	0.14542 (116)
C(2)	−0.00041 (354)	0.15496 (149)	0.08509 (151)
C(3)	0.13652 (477)	0.46441 (149)	0.35453 (108)
C(4)	0.34375 (434)	0.42026 (178)	0.36041 (131)
C(5)	0.23020 (343)	0.06138 (131)	0.47495 (113)
C(6)	0.30442 (414)	−0.03023 (133)	0.37446 (126)
$H_2O(1)$	−0.16214 (312)	−0.18750 (127)	0.19783 (109)
$H_2O(2)$	−0.25156 (536)	0.46115 (360)	0.13712 (228)
$H_2O(3)$	0.32165 (418)	−0.34451 (185)	0.17396 (134)
$H_2O(4)$	0.39392 (361)	0.35142 (159)	0.06068 (153)
$H_2O(5)$	0.06670 (1000)	0.47500 (500)	0.00800 (500)

[a] $10^5\sigma$ in parentheses.

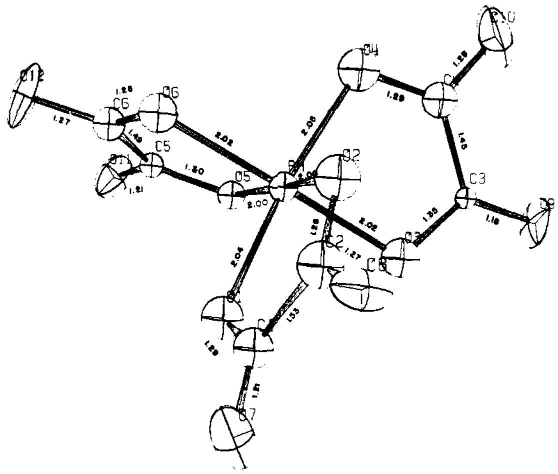

Figure 1. Tris(oxalato)rhodate(III) anion.

In the tris(oxalato)rhodate(III) ion (see Figure 1), the Rh(III) is coordinated to six oxygen atoms in a somewhat distorted octahedron. The average Rh-O distance is 2.016 Å (range 2.000–2.046 Å), and the deviations from the average are not considered significant. The angles O-Rh-O deviate considerably from the octahedral values of 90 and 180°. For neighboring oxygen atoms, the O-Rh-O angles range from 81.6 to 95.8°, and the lowest value for the angle for opposite oxygen atoms is 172.1°. Thus the octahedron is angularly distorted, as can be expected because of the bis-chelated oxalato groups. In fact, all O-Rh-O angles involving oxygen atoms of the same oxalato group are much less than 90°, their average value being 82.88°. The weighted average distances C—C, C—O, and C=O are 1.495, 1.290, and 1.233 Å, respectively. Calculation of least-squares planes in the complex ion shows that the oxalato groups O_2CCO_2 are not coplanar with the plane RhO_4 formed by rhodium and four inner oxygen atoms, the dihedral angles ranging from 5.12 to 10.95°.

All potassium ions are seven-coordinated, to water molecules (weighted average distance 2.847 Å) and oxygen atoms of the oxalato groups (weighted average distance 2.804 Å). Of the three crystallographically different potassium ions, two are similar, *viz.*, K(1) and K(3), in that they are both coordinated to three water molecules, three outer (carbonyl) oxygens, and one inner carbonyl oxygen. K(1) links three anions, while K(3)

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(4) Potassium tris(oxalato)rhodate(III) was provided by H. G. Kruszyna. The preparation, analysis, and storage of the sample have been described: M. W. Hsu, H. G. Kruszyna, and R. M. Milburn, *Inorg. Chem.*, **8**, 2201 (1969).

(5) The structure factor table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

links four anions together. The third potassium ion, K(2), is unusual because, while it is also coordinated to three outer oxalato oxygens, it is not coordinated to water but instead to four inner oxalato oxygens, three of which are in the same anion. K(2) is thus located directly above a triangular plane of the coordination octahedron of rhodium, resulting in a very short Rh–K distance of 3.480 Å. This distance may be compared to the average Rh–O distance to the outer oxygen atoms in the same anion of 3.957 Å. This phenomenon of K^+ penetrating into the coordination sphere of the anion had been observed previously in the structures of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$,[6] $K_3[Ir(C_2O_4)_3]\cdot 2H_2O$,[7] and $K_3[Rh(C_2O_4)_3]\cdot 2H_2O$.

The water molecules are tetrahedrally surrounded. There are five crystallographically independent water molecules in the structure, which can be differentiated into three kinds: (a) $H_2O(1)$ and $H_2O(3)$ are surrounded by two potassium ions and two oxygen atoms (or other water molecules); (b) $H_2O(2)$ and $H_2O(4)$ are surrounded by one potassium ion and three oxygen atoms (or other water molecules); and (c) $H_2O(5)$, which represents the 0.5 H_2O in the stoichiometric formula and is found to be statistically disordered, is surrounded by four water molecules.

The structure reported here is capable of providing an alternative interpretation of the nmr and dehydration results noted above, and the reaction kinetics of the complex can be explained[8] without the assumption of a monoaquated species preexisting in the solution.

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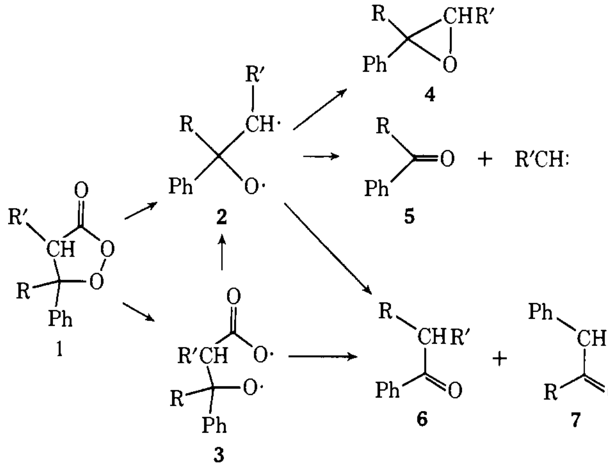
Cyclic Peroxides. VI.[1] Oxatrimethylene Diradicals *via* Photodecarboxylation of β-Peroxylactones[2]

Sir:

In view of the fact that photodecarboxylation of malonoyl peroxide[1] leads to α-lactones and mercury-sensitized photolysis of γ-butyrolactone[3] produces trimethylene diradicals which preferentially cyclize into cyclopropane, it was expected that β-peroxylactone **1** should photodecarboxylate to give the 1-oxatrimethylene diradical **2**. Diradical **2** should cyclize into epoxide **4**, but alternatively it could fragment into ketone **5** and methylene or rearrange into ketones **6** (alkyl migration) and **7** (phenyl migration), as illustrated in eq 1.[4] In this communication we report on the photolysis of peroxylactones **1a** (R = Me; R′ = H) and **1b** (R = Ph; R′ = Me) and show that indeed the oxatrimethylene diradical **2** is the precursor to the photoproducts rather than the 3-keto-1,5-dioxapentamethylene diradical **3**.[5]



(1)

The volatile products of the photolysis[6] of **1a** are summarized in Table I. Also, approximately 20% of unidentified residue was formed, providing a product balance of better than 96%. Control experiments showed that epoxide **4a** and ketones **5a**, **6a**, and **7a** were stable toward the photolysis conditions of **1a**, indicating that these photoproducts are primary products and do not interconvert during photolysis. Furthermore, photolysis of **1a** in the presence of each of the photoproducts did not alter the proportions of the products, suggesting that no photosensitized decomposition of **1a** by the products took place. Molecular oxygen had no effect on the product composition. When the photolysis was carried out in benzene which contained 1 *M* amounts of piperylene, the same products were formed (Table I).

The photolysis of (*S*)-(−)-**1b**, for which the preparation and configurational assignment were described previously,[5] gave 1,1-diphenylepoxypropane (**4b**), benzophenone (**5b**), α-methyldeoxybenzoin (**7b**), and benzhydryl methyl ketone (**8**), besides major amounts of intractable residue. It proved difficult to isolate epoxide **4b** and for that reason all volatile components were sublimed directly out of the photolysis mixture, the sublimate hydrolyzed with 0.1 *N* perchloric acid, and the 1,1-diphenyl-1,2-propanediol (**9**) isolated by fractional crystallization. Within experimental error, diol **9** and ketone **7b**, the only potentially optically active volatile photoproducts, showed zero rotation. For the purpose of control experiments to test the photostability of epoxide **4b**, the latter was prepared by converting (*R*)-(−)-*n*-butyl lactate to diol **9**, mp 92.5–93.5°, $[\alpha]^{26}D$ −150.2° in benzene (lit.[7] mp 92–93°, $[\alpha]^{26}D$ −149.8° in benzene) by treatment with excess phenylmagnesium bromide. The monobenzenesulfonate of diol **9** (mp 82–83°, $[\alpha]^{26}D$ −32.8° in benzene), prepared in 75% yield by treatment of **9** with benzenesulfonyl chloride in pyridine, on reaction with sodium hydride in dimethoxyethane gave a 76% yield of epoxide **4b** (mp 64–65°, $[\alpha]^{26}D$ +21.7° in benzene). To check the configuration and optical purity of **4b**, the latter

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(1) Part V: W. Adam and R. Rucktäschel, *J. Amer. Chem. Soc.*, **93**, 557 (1971).

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