

While the observed rate constants for inner oxygen exchange and racemization are remarkably similar at 56.3°, the activation parameters appear to be significantly different (Table I). This implies the rates for the two processes would become quite dissimilar at tem-

Table I. Kinetic Data on Acid-Catalyzed Oxygen Exchange, Racemization, and Aquation for $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$

	Ionic strength	$k_2 \times 10^6, M^{-1} \text{sec}^{-1}{}^{17}$	$\Delta H^\ddagger, \text{kcal mole}^{-1}$	$\Delta S^\ddagger, \text{eu}$
Outer oxygens	0.54	9.2 (25.1°)	16.9 (± 2) ^a	-20 (± 6)
Inner oxygens	0.54	8.4 (56.3°)	23.6 (± 2) ^b	-6 (± 6)
		0.24	10.2 (56.3°)	
Racemization ^c	0.23 ^c	14.2 ^d (56.3°)	19.4 (± 1) ^e	-18 (± 3)
Aquation	0.23	0.68 ^f (56.3°)	26.4 (± 1) ^g	-2 (± 3)

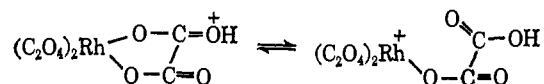
^a From $T = 25.1, 45.0, \text{ and } 56.3^\circ$. ^b From $T = 45.0, 56.3, \text{ and } 67.0^\circ$. ^c Calculated from data in ref 18. ^d A corrected value which is $(2.303)^2$ times the value reported. ^e Measured at ionic strength 3.0. ^f Measured by us using the method of ref 15. ^g From ref 15b for ionic strength 1.00, with our estimate of error limits.

Table II. Acid-Catalyzed Oxygen Exchange for Three Ions of Type $\text{M}(\text{C}_2\text{O}_4)_n^{m-}$

Oxalato species	Ionic strength	$k_2 \times 10^4 (25^\circ), M^{-1} \text{sec}^{-1}{}^{17}$	$\Delta H^\ddagger, \text{kcal mole}^{-1}$	$\Delta S^\ddagger, \text{eu}$
HC_2O_4^- ^a	0.055	2.6	14.4 (± 1.5)	-28 (± 4)
$\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ ^a	0.020	3.5	14.1 (± 1)	-27 (± 3)
$\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$				
Outer oxygens	0.070	2.2	16.9 (± 2) ^b	-19 (± 6)

^a From ref 2. ^b Measured at ionic strength 0.54.

peratures significantly removed from $\sim 56^\circ$. However, a nonidentity of observed activation parameters does not rule out the possibility that both processes proceed through a common intermediate, such as a monodentate oxalato species,^{1,20} e.g.



This is because the additional but different processes required to consummate inner oxygen exchange and racemization could contribute to the measured rate constants and activation parameters for the over-all reactions.

(20) H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 1743 (1967).

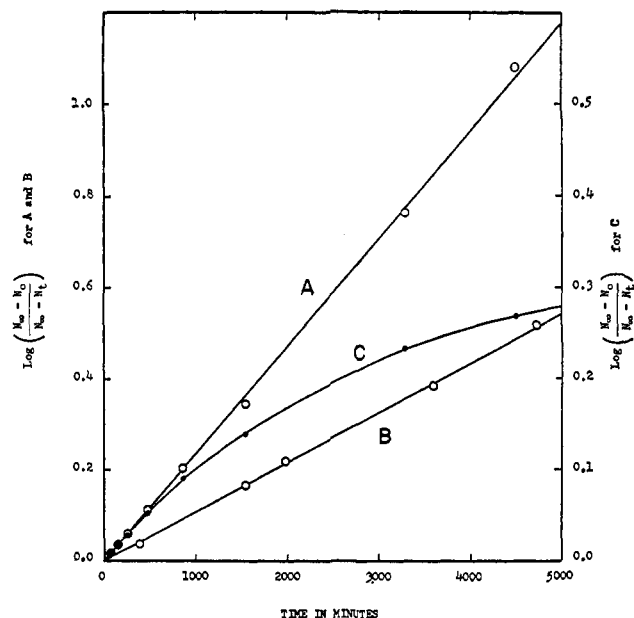


Figure 1. Oxygen exchange in $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$ at ionic strength 0.54. (A) Outer oxygens at 25.1°, $[\text{H}^+] = 0.0978 \text{ M}$, $[\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}] = 0.0100 \text{ M}$; N_0 is for natural abundance and N_∞ for equilibration of 6 oxygens.⁷ (B) Inner oxygens at 45.0°, $[\text{H}^+] = 0.205 \text{ M}$, $[\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}] = 0.0100 \text{ M}$; N_0 and N_∞ are for equilibration of 6 and 12 oxygens, respectively. (C) Data as for A, with $N_0 =$ natural abundance, and N_∞ assuming equilibration of all 12 oxygens.

We are continuing our investigations in an effort to resolve some of these interesting problems.

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Dichlorocyclopropenone

Sir:

Tetrachlorocyclopropene (**1**) reacts with aluminum chloride to form the salt trichlorocyclopropenium tetrachloroaluminate (**2**).¹ Quenching of **2** with water regenerates **1**.² We now find that very slow hydrolysis of a suspension of **2** in methylene chloride produces an aluminum complex (**3**) from which dichlorocyclopropenone (**4**), the first dihalocyclopropenone, can be isolated as a dangerously unstable liquid.

As a stirred methylene chloride suspension of **2** absorbs moisture from the atmosphere, the insoluble salt gradually dissolves to a clear solution. Evaporation of the solvent affords a viscous residue which slowly crystallizes to a colorless solid, **3**: mp 103–106°; ν_{max} (CH_2Cl_2) 1860 and 1545 cm^{-1} . A satisfactory analysis could not be obtained, but the properties of this solid suggest that it is an aluminum chloride complex of **4**. The solid was redissolved in methylene chloride, cooled

(1) S. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964); R. West, A. Sadō, and S. Tobey, *ibid.*, **88**, 2488 (1966).

(2) S. Tobey and R. West, *Tetrahedron Letters*, 1179 (1963).

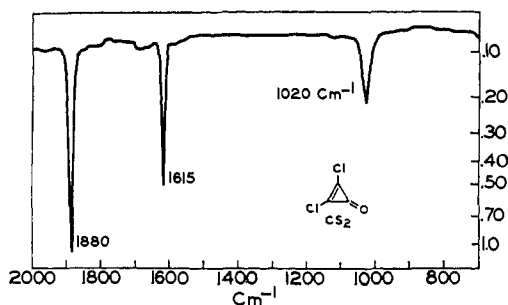
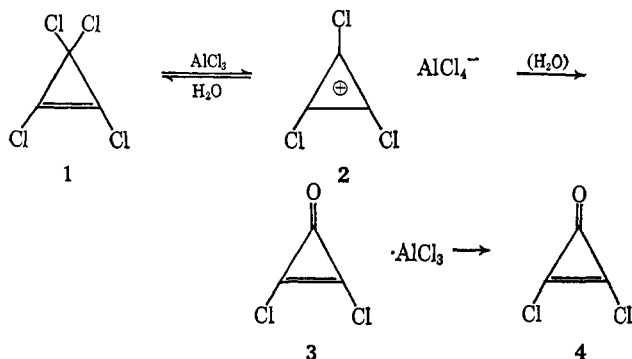


Figure 1. Infrared spectrum of dichlorocyclopropenone in CS_2 .

to 0–5°, and shaken for a few seconds with ice water. The organic layer was separated, dried over calcium chloride and magnesium sulfate at 0°, and then concentrated under vacuum. Molecular distillation of



the residue (0°, 0.05 mm) under nitrogen followed by repeated crystallization from pentane at –40° gave pure colorless dichlorocyclopropenone: mp –6°; m/e 122. Calcd for 2Cl : P + 2, 65.3%; P + 4, 10.6%. Found: P + 2, 62.5%; P + 4, 10.1%.³ Besides the parent peak, five major fragment peaks appeared in the mass spectrum of **4**, corresponding to loss of Cl, Cl_2 , CO, COCl, and C_2ClO . No proton resonance appeared in the nmr spectrum. The infrared spectrum (Figure 1) contained strong bands at 1880 and 1615 cm^{-1} in the region characteristic of substituted cyclopropenones.^{4,5} An additional band at 1020 cm^{-1} is probably due to C–Cl modes of the vinylic chlorine.²

On one occasion a large sample of **4** (~40 g), after being crudely distilled and stored overnight at –78°, underwent detonation while being warmed to room temperature prior to further purification. Preparation of **4** only in quantities less than 1 g and use of appropriate shielding is recommended. Amounts of **4** up to 1 g have been prepared repeatedly and have never decomposed explosively at temperatures below 0°. Dilute solutions of **4** in CH_2Cl_2 can be handled at room temperature, where they appear to have a decomposition half-time of a few hours.

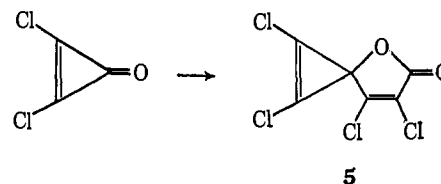
The neat liquid decomposes rapidly, and sometimes explosively, at room temperature. Molecular distillation of the dark residue after decomposition gave about

(3) R. Silverstein and G. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., p 17.

(4) (a) A. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965); (b) R. Breslow, L. Altman, A. Krebs, E. Mohacsi, I. Murata, R. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320, 1326 (1965); (c) R. Breslow and L. Altman, *ibid.*, **88**, 504 (1966); (d) D. Farnum, J. Chickos, and P. Thurston, *ibid.*, **88**, 3075 (1966).

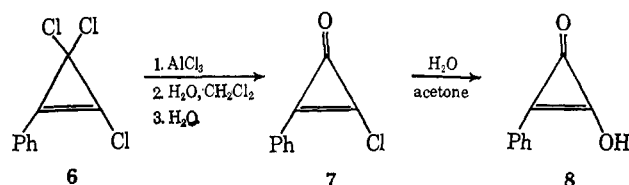
(5) The parent compound, cyclopropenone, exhibits absorptions at 1835 and 1870 cm^{-1} : R. Breslow and G. Ryan, *ibid.*, **89**, 3073 (1967).

20% of a crystalline dimer: mp 75–76°; ν_{max} (CS_2) 1820, 1795, 1625, 1005, and 930 cm^{-1} . *Anal.* Calcd for $(\text{C}_3\text{Cl}_2\text{O})_2$: C, 29.31; Cl, 57.68%; mol wt, 244. Found: C, 29.34; Cl, 57.67, m/e 244. Calcd for 4Cl : P + 2, 131%; P + 4, 63.9%. Found: P + 2, 126%; P + 4, 63.3%. The dimer is believed to have the spiro lactone formula **5**. Thermal dimerization of cyclopropenones to spiro lactones of this type is well known.⁴



Further hydrolysis of **4** with 65% aqueous sulfuric acid leads to α,β -dichloroacrylic acid, isolated in high yield and identical with that obtained earlier by aqueous hydrolysis of **1**.²

The generality of the slow hydrolysis reaction as it pertains to the synthesis of other cyclopropenones is shown by the conversion of phenyltrichlorocyclopropenone (**6**)⁶ to chlorophenylcyclopropenone (**7**): mp 40–43 dec; ν_{max} (CS_2) 1865, 1640, and 1220 cm^{-1} ; nmr multiplet centered at τ 2.3; m/e 164. Calcd for 1Cl : P + 2, 32.6%. Found: P + 2, 34.2%. Hydrolysis of **7** in aqueous acetone afforded the known compound^{4d} hydroxyphenylcyclopropenone (**8**) in high yield. Hydrolysis of other chlorocyclopropenones is under investigation.



Acknowledgment. This research was supported by a grant from the Public Health Service.

(6) S. Tobey and R. West, *ibid.*, **86**, 4215 (1964); J. Chickos, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1966; D. Zecher, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1967.

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Solvent Effects on the Values Measured for Enthalpies of Adduct Formation

Sir:

We have been interested in obtaining and interpreting thermodynamic data for the formation of 1:1 Lewis acid–base adducts.¹ Linear relationships have been shown to exist between the measured enthalpies and parameters obtained from infrared and nmr data^{2–4} for certain systems. Ideally these enthalpies of adduct formation should involve unsolvated, monomolecular species which would be best approximated by gas-phase

(1) For a review and discussion of previous work, see R. S. Drago, *Chem. Brit.*, 3516 (1967).

(2) T. D. Epley and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 5770 (1967).

(3) M. D. Joesten and R. S. Drago, *ibid.*, **84**, 3817 (1962).

(4) T. F. Bolles and R. S. Drago, *ibid.*, **88**, 5730 (1966).