most stable ion can be observed, protonated nortricyclene must represent a lower energy level species than the norbornyl cation. Based on previous nmr studies, it was suggested that the 3,2-hydride shift in the norbornyl cation is relatively slow ($\Delta F^{\ddagger} \sim 11$ kcal/mol in SbF_5–SO_2) and can be frozen out in contrast with the exceedingly fast ($\Delta F^{\ddagger} < 5.0$ kcal/mol) exchange of the 1, 2, and 6 hydrogen atoms. The observed barrier for the slow 3,2-hydride shift does not appear to be in agreement with other secondary–secondary hydride shifts. It is therefore reasonable to suggest that the activation energy barrier observed in the nmr spectra also includes the energy difference I $\rightarrow$ II. Thus, the 3,2-hydride shift would take place in the norbornyl cation II, and not in ion I, where it is not favored. Rapid scrambling of hydrogens 1, 2, and 6, on the other hand, is possible in I.

Our study demonstrates the great power of laser-based Raman spectroscopy in the structural determination of carbonium ions, particularly when differentiation of potentially fast equilibrating systems from bridged ions is involved.

Acknowledgment. Support of the work by the National Science Foundation and the Petroleum Research Fund is gratefully acknowledged.

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Oxygen Exchange between Tris(oxalato)rhodate(III) Ion and Solvent Water. Exchange of Outer and Inner Oxygens

Sir:

Acid-catalyzed oxygen exchange between complexes of the type $M(C_2O_4)_n{}^{n-}$ and water has been examined previously[1,2] for $Cr(C_2O_4)_3{}^{3-}$, $Co(C_2O_4)_3{}^{3-}$, and $Pt(C_2O_4)_2{}^{2-}$. For each of these ions, all 4*n* oxygens exchange, under fixed conditions, at apparently indistinguishable rates. Similar results were observed for oxalic acid.[1–4] In contrast, we find that $Rh(C_2O_4)_3{}^{3-}$ in acidic media exchanges one-half of its oxygens significantly more rapidly than the other half. The result is of particular interest because of possible relationships between racemization and oxygen exchange for this ion and related complexes.

Reaction solutions were prepared from solutions containing $Na_3Rh(C_2O_4)_3$,[5] $HClO_4$, $NaClO_4$, and O^{18} enriched water. Aliquots were quenched with cooled $AgNO_3$, and the precipitated $Ag_3Rh(C_2O_4)_3$ was dried and thermally decomposed to Ag, Rh, and CO_2. The CO_2 46/(44 + 45) ratios were measured with a Nuclide 6-60-RMS 2 mass spectrometer.

Linear first-order rate plots[6] for the early stages of reaction are obtained only if one uses for the infinity value the O^{18} enrichment expected if very close to one-half of the oxygens have equilibrated with solvent (Figure 1A).[7] Such plots provide pseudo-first-order rate constants which we associate with exchange of outer oxygens. After the outer oxygens have equilibrated with solvent, inner oxygen exchange can be followed. Linear first-order plots are obtained here if one takes as the initial time the point when one-half of all oxygens have equilibrated[9] (Figure 1B). A modified McKay equation for the case where one-half the atoms exchange at one rate and one-half at a different rate gives linearity for 90% of all oxygens.[1,10] For both inner and outer oxygens, exchange rates are first order in both complex and hydrogen ion concentrations. Arrhenius plots show good linearity for each kind of oxygen. At 25° outer oxygens exchange ~60 times more rapidly than inner oxygens; at 56° the difference is ~20-fold. Thus we have usually equilibrated the outer oxygens at 25° before following inner oxygen exchange at higher temperatures. That there are kinetically distinguishable oxygens in $Rh(C_2O_4)_3{}^{3-}$ and not in the Cr(III), Co(III), and Pt(II) analogs[11] is a reflection of the considerable inertness of the rhodium–oxygen bonds.[13,14] While slow, inner oxygen exchange in $Rh(C_2O_4)_3{}^{3-}$ is considerably more rapid under comparable conditions than aquation to give free oxalate.[15,16]

Table I summarizes our results[17] on oxygen exchange and available data on the racemization[18] and aquation[15] of the $Rh(C_2O_4)_3{}^{3-}$ ion. A comparison with our earlier results[2] is in Table II.

Based on studies of $Pt(C_2O_4)_2{}^{2-}$ and $HC_2O_4{}^-$ it was predicted,[2] as a first approximation, that under comparable acidic conditions all nonlabile oxalato complexes of type $M(C_2O_4)_n{}^{n-}$ will exchange oxygen at similar rates. Our results for $Rh(C_2O_4)_3{}^{3-}$ are in accord with this idea (Table II). Outer oxygen exchange in $Rh(C_2O_4)_3{}^{3-}$ is therefore considered to proceed by the previously suggested A2 mechanism.[19]

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[1] C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4615 (1964).

[2] (a) J. E. Teggins and R. M. Milburn, Abstracts of Papers, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964 p 13-O; (b) *Inorg. Chem.*, 4, 793 (1965).

[3] R. M. Milburn and H. Taube, *J. Amer. Chem. Soc.*, **81**, 3515 (1959).

[4] C. O'Connor and D. R. Llewellyn, *J. Chem. Soc.*, 2197 (1965).

[5] Prepared from $K_3Rh(C_2O_4)_3 \cdot 1.5H_2O$ kindly provided by Dr. Harriet Kruszyna.

[6] The rate equation may be written $\log [(N_\infty - N_0)/(N_\infty - N_t)] = (k/2.303)t$, where N = atom fraction of O^{18}.

[7] If for N_∞ one assumes $^{13}/_{24}$ of the oxygen has equilibrated, as might be suggested by the formulation of $K_3Rh(C_2O_4)_3 \cdot 4.5H_2O$ proposed by Porte, *et al.*,[8] the points lie closer to a straight line for slightly longer reaction times.

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

[9] Thus N_0 for inner oxygen exchange = N_∞ for outer oxygen exchange.

[10] A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, p 13.

[11] For the cationic complexes $Co(NH_3)_4C_2O_4{}^+$ and $Co(NH_3)_5C_2O_4H^{2+}$, however, kinetically distinct oxygens have been observed.[12]

[12] (a) R. B. Jordan, C. A. Andrade, and H. Taube, Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, 1964, pp 381–394; (b) C. Andrade, R. B. Jordan, and H. Taube, Abstracts of Papers, 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, p 13-M.

[13] R. W. Olliff and A. L. Odell, *J. Chem. Soc.*, 2417 (1964).

[14] R. G. Pearson in "Some Aspects of Crystal Field Theory," T. M. Dunn, D. S. McClure, and R. G. Pearson, Ed., Harper and Row, New York, N. Y., 1965, p 106.

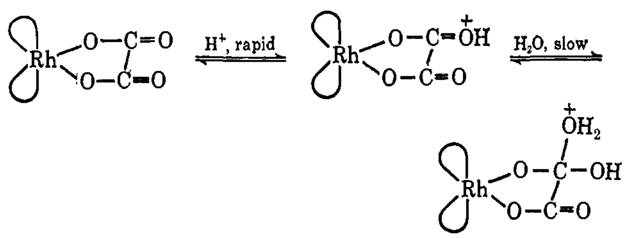
[15] (a) D. Barton and G. M. Harris, *Inorg. Chem.*, **1**, 251 (1962); (b) K. V. Krishnamurty, *ibid.*, **1**, 422 (1962).

[16] For 56° we estimate that the enrichment in the CO_2 arising through exchange in freed oxalate can be no more than ~3% of that attributable to the inner oxygen exchange.

[17] $k_2 = k_1/[H^+]$.

[18] A. L. Odell, R. W. Olliff, and F. B. Seaton, *J. Chem. Soc.*, 2280 (1965).

[19] For oxygen exchange in $Cr(C_2O_4)_3{}^{3-}$, $Co(C_2O_4)_3{}^{3-}$, and $H_2C_2O_4$, Bunton, *et al.*,[1] also observed similar kinetic parameters and proposed an A2 type mechanism. Their mechanism differs from ours in that it requires a ring opening before *any* oxygens can exchange. The quantitative results are difficult to include in the present comparison because of widely differing ionic strengths.



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 temperatures significantly removed from ~56°. 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.*

Table I. Kinetic Data on Acid-Catalyzed Oxygen Exchange, Racemization, and Aquation for $Rh(C_2O_4)_3^{3-}$

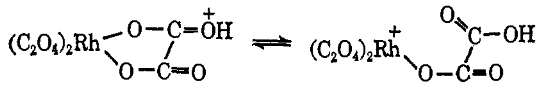
	Ionic strength	$k_2 \times 10^5$, M^{-1} sec^{-1} [17]	$\Delta H^\ddagger$, kcal mole^{-1}	$\Delta S^\ddagger$, eu
Outer oxygens	0.54	9.2 (25.1°)	16.9 (±2)[a]	−20 (±6)
Inner oxygens	0.54	8.4 (56.3°)	23.6 (±2)[b]	−6 (±6)
	0.24	10.2 (56.3°)		
Racemization[c]	0.23[c]	14.2[d] (56.3°)	19.4 (±1)[e]	−18 (±3)
Aquation	0.23	0.68[f] (56.3°)	26.4 (±1)[g]	−2 (±3)

[a] From T = 25.1, 45.0, and 56.3°. [b] From T = 45.0, 56.3, and 67.0°. [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 $M(C_2O_4)_n^{n-}$

Oxalato species	Ionic strength	$k_2 \times 10^4$ (25°), M^{-1} sec^{-1} [17]	$\Delta H^\ddagger$, kcal mole^{-1}	$\Delta S^\ddagger$, eu
$HC_2O_4^-$ [a]	0.055	2.6	14.4 (±1.5)	−28 (±4)
$Pt(C_2O_4)_2^{2-}$ [a]	0.020	3.5	14.1 (±1)	−27 (±3)
$Rh(C_2O_4)_3^{3-}$ Outer oxygens	0.070	2.2	16.9 (±2)[b]	−19 (±6)

[a] From ref 2. [b] Measured at ionic strength 0.54.



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.

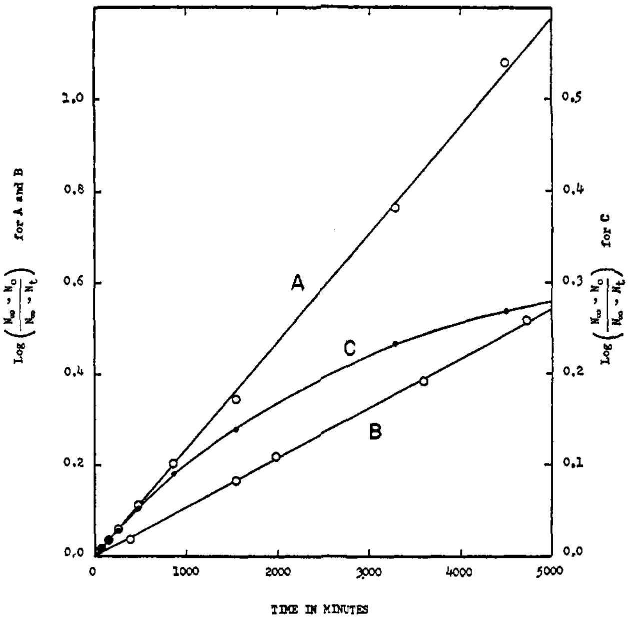


Figure 1. Oxygen exchange in $Rh(C_2O_4)_3^{3-}$ at ionic strength 0.54. (A) Outer oxygens at 25.1°, $[H^+]$ = 0.0978 M, $[Rh(C_2O_4)_3^{3-}]$ = 0.0100 M; N_0 is for natural abundance and N_∞ for equilibration of 6 oxygens.[7] (B) Inner oxygens at 45.0°, $[H^+]$ = 0.205 M, $[Rh(C_2O_4)_3^{3-}]$ = 0.0100 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.

Acknowledgment. We are grateful to the National Science Foundation for support under Grant GP-6383 and for Grant GP-5561 with which the mass spectrometer was obtained.

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Received February 19, 1968

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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

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

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