1-Methyl-3-phospholene 1-oxide (I)[8] was converted to its dibromide (II).[8] This was reduced to the phospholane (III) by a 3-hr reflux of a benzene solution of the oxide (0.153 mole) and trichlorosilane[9] (0.43 mole). After acid hydrolysis and basification with sodium bicarbonate, the product was extracted continuously with pentane. By an iodine titration the yield in this step was found to be about 65%. Some III crystallized from a concentrated solution and had mp 47.5–49°. The benzyl bromide salt, recrystallized from ethyl acetate, had mp 171.5–172.5°. *Anal.* Calcd for $C_{12}H_{16}Br_3P$: C, 33.52; H, 3.75; P, 7.20. Found: C, 33.56; H, 3.75; P, 7.40. The proton nmr spectrum ($CDCl_3$) of III was in accord with the structure [3 H doublet ($J = 4$ cps) at δ 0.70 ppm, 4 H multiplet at 1.87, 2 H multiplet at 3.98].

III was dehydrohalogenated in pentane with 3 molar equiv of potassium *t*-butoxide at room temperature overnight. The cooled mixture was hydrolyzed with sodium bicarbonate solution and extracted with pentane. By gas chromatography the yield of IV was 24%. Some 1-methyl-3-phospholene was present as an impurity, but was largely extracted with 0.5 *N* hydrochloric acid without affecting IV. The phosphole in neat or concentrated form is sensitive to prolonged heating, and fractionation is accompanied by considerable loss. However, a sample of 87.8% purity (pentane as the main impurity) was obtained as the heart-cut in a rapid, direct distillation of the residue left from removing the solvent at 300 mm with a spinning-band column. The sample was collected at 82–85° (317 mm) in a receiver chilled in Dry Ice. As it discolors slightly at room temperature, forming a small amount of insolubles, the sample is best preserved at low temperatures. It readily formed a methiodide, which was recrystallized (low recovery) from methanol–ethyl acetate, mp 190–194° dec. *Anal.* Calcd for $C_6H_{10}IP$: C, 30.02; H, 4.20; P, 12.91; I, 52.87. Found: C, 30.15; H, 4.39; P, 12.63; I, 52.63.

The 60-Mc proton nmr spectrum (external standard) of IV (87.8%) consists of a methyl signal as an apparent singlet (any PCH coupling must be less than about 1 cps) at δ 1.36 ppm and a 4 H multiplet for the vinyl protons at 6.51–7.52 ppm. The multiplet is being analyzed as A_2B_2 in an A_2B_2X system where P^{31} is X; coupling parameters will be reported elsewhere. Preliminary calculations suggest that the α and β protons differ in chemical shift by about 8 cps, and that $J_{AX} + J_{BX} = 54$ cps. The P^{31} nmr spectrum at 40.5 MHz is an 11-line pattern at +121 ppm relative to external P_4O_6 standard (*cf.* +154.3 ppm for 1-methyl-3-phospholene).

The α- and β-proton multiplet, centered at 7.09 ppm, is at markedly lower field than in vinylphosphines. For comparison, data reported[10] for neat trivinylphosphine (recalculated to δ) place the α proton at 6.66, and the β protons at 5.69 (*trans* to P) and 5.56 ppm (*cis* to P). Also the vinyl proton in neat 1-phenyl-3-methyl-2-phospholene is observed at δ 5.68 ppm (internal TMS).[11] The ring protons of IV resonate in the range characteristic of those of aromatic systems (*e.g.*, for neat thiophene, α and β are at 7.04 and 6.92 ppm, respectively, to internal TMS[12]). A similar downfield position for the β protons of 2,5-dimethyl-1-phenylphosphole (6.39 ppm)[5] and of 1,2,5-triphenylphosphole (7.1–7.6 ppm, unresolved from phenyl protons)[6] has been observed.

The ultraviolet spectrum of 1-methylphosphole in isooctane (λ_{max} 286 mμ (log ϵ 3.88); intense end absorption at 200 mμ) resembles that of 1-methylpyrrole (λ_{max} 280 mμ (log ϵ 2.06) and 214 mμ (log ϵ 3.77)). The mass spectrum shows a strong molecular ion at *m/e* 98 and a breakdown pattern similar to that of 1-methylpyrrole.

Although IV quaternizes with the usual ease and has an exceptionally strong phosphine odor, its basicity appears to be abnormally low for a tertiary phosphine. As noted, it is not extracted from pentane by 0.5 *N* hydrochloric acid. It is extracted by 4 *N* hydrochloric acid, but with chemical change, as it is not recovered on basification. A dilute (10^{-4} *M*) solution in 0.01 *N* hydrochloric acid is also unstable, as seen by the gradual reduction in the absorbance at 285 mμ. The phosphole differs from other tertiary phosphines also in not forming a complex with carbon bisulfide. These chemical properties, as well as the proton nmr and ultraviolet spectral properties, may be indicative of the expected[3] extensive electron delocalization of an aromatic system. A final judgment in this matter, however, must await the results of other experiments on the properties of the system and a comparison of the properties with vinylic, but nonaromatic, phosphines.

Acknowledgment. We thank Dr. Charles Moreland, North Carolina State University, Raleigh, N. C., for obtaining the P^{31} nmr spectrum of IV and for preliminary calculations on its proton nmr parameters.

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(8) L. D. Quin, J. A. Peters, C. E. Griffin, and M. Gordon, *Tetrahedron Letters*, 3689 (1964).

(9) H. Fritzsche, U. Hasserodt, and F. Korte, *Ber.*, **98**, 171 (1965).

(10) W. A. Anderson, R. Freeman, and C. A. Reilly, *J. Chem. Phys.*, **39**, 1518 (1963).

(11) L. D. Quin and T. P. Barket, unpublished results.

(12) T. F. Page, Jr., T. Alger, and D. M. Grant, *J. Am. Chem. Soc.*, **87**, 5333 (1965).

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The Solvolysis of (7-Cycloheptatrienyl)methyl 3,5-Dinitrobenzoate. An Example of Cyclopropane Participation Initiated by Valence Tautomerism

Sir:

Extensive investigation has demonstrated that carbon–carbon bonding electrons of various types can function as nucleophilic neighboring groups in intramolecular displacement reactions.[1-14] Some evidence

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(1) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; *Chem. Rev.*, **56**, 571 (1956).

(2) B. Capon, *Quart. Rev.* (London), **18**, 45 (1964).

(3) M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965).

(4) J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

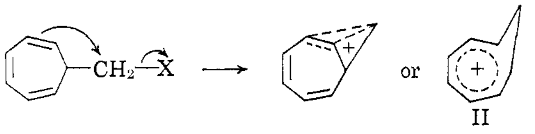
(5) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms 1965," Interscience Publishers, Inc., New York, N. Y., 1966, Chapter 1; B. Capon and C. W. Rees, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **61**, 222 (1964).

(6) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

(7) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959), and references therein cited.

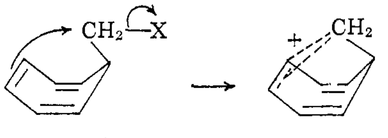
also exists for similar participation by carbon–hydrogen bonding electrons.[1-3] As yet, no clear definition of the factors which influence the relative efficiency of nucleophiles within this class has emerged; in fact, even the qualitative order of nucleophilicity is not well established. The solvolysis of derivatives of 7-hydroxymethylcyclopheptatriene (Ia) provides a unique opportunity to observe simultaneous internal competition between five different types of bonding electron nucleophile.

Homoallylic π-electrons[1-5,7,8,14]



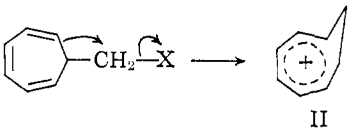
(1)

Remote π electrons[1-6,9,15]



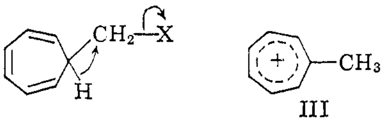
(2)

Carbon–carbon σ electrons[1-6]



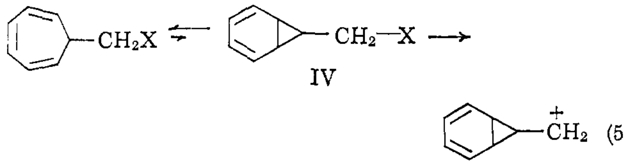
(3)

Carbon–hydrogen σ electrons[1,2,4]



(4)

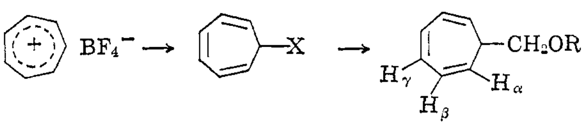
Cyclopropane carbon–carbon σ electrons[1-3,10-13]



(5)

Process 1 finds analogy in the solvolysis of 6-(1,4-cyclohexadienyl)methyl *p*-toluenesulfonate[14] (VIII) which is accelerated by a factor of *ca.* 100 over that of cyclohexylmethyl *p*-toluenesulfonate (Table I). Process 2 is observed in the solvolysis of Δ^4-cycloheptenylmethyl *p*-bromobenzenesulfonate (IX), which undergoes acetolysis at a rate enhanced by a factor of *ca.* 60 over that of cycloheptylmethyl *p*-bromobenzenesulfonate (VII).[15] Processes 3 and 4 might prove particularly facile in this system, since each results in the formation of a cationic intermediate to which one attributes special stability: the homotropylium (II)[16] and methyltropylium (III)[17] cations, respectively. Process 5 would require initial conversion of I to its norcaradiene valence tautomer (IV),[18] a cyclopropylcarbinyl derivative. The ability of cyclopropane to stabilize adjacent incipient cationic centers is well documented,[1-3,10-13] although the nature of the interaction remains a topic of considerable discussion.[13]

Our efforts to obtain pure 7-hydroxymethylcycloheptatriene (Ia) by the method previously described[19] led, instead, to a complex mixture of products including, among others, Ia, isomeric hydroxymethylcycloheptatrienes, and 2-phenylethanol. Pure 7-hydroxymethylcycloheptatriene was synthesized by $LiAlH_4$ reduction of 7-cycloheptatrienecarboxylic acid (VIc), which was prepared by the procedure of Dauben (V → VIa → VIb → VIc).[20] The structural integrity of Ia is established beyond question by its nmr spectrum (CCl_4): τ 3.45 (triplet, H_γ), 3.85 (multiplet, H_β), 4.8 (four-line multiplet, H_α), 6.15 (doublet, CH_2O), 6.3 (singlet, OH), 8.13 (multiplet, CH), in the ratio 1.83: 1.92:1.92:2.0:1.0:1.0.



V

VIa, X = CN
VIb, X = $CONH_2$
VIc, X = COOH

Ia, R = H
Ib, R = $C_6H_3(NO_2)_2COO$

Treatment of Ia with 3,5-dinitrobenzoyl chloride in pyridine gave Ib (mp 67–68°; *Anal.* Calcd for $C_{15}H_{12}N_2O_6$: C, 68.8; H, 2.76; N, 6.43. Found: C, 68.8; H, 2.84; N, 6.36), whose nmr spectrum verifies that no rearrangement accompanies esterification. The solvolysis of Ib in 60% aqueous acetone is cleanly first order through three half-lives with k_1 (100°) = 2.6×10^{-6} sec^{-1} and k_1 (125°) = 3.0×10^{-5} sec^{-1} ($\Delta H^{\ddagger}$ = 28.3 kcal/mole, $\Delta S^{\ddagger}$ = −8.9 eu).

Reference to Table I demonstrates that the solvolytic reactivity of Ia is enhanced by a factor of *ca.* 5.5×10^5 over that of its fully saturated analog, cycloheptyl-

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(8) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 3773 (1964), and references therein cited.

(9) (a) For citations to pertinent literature, see F. C. Uhle, *J. Org. Chem.*, 31, 4193 (1966), footnote 26; (b) for a review, see G. D. Sargent, Ph.D. Thesis, Harvard University, 1964, Chapter 2; *Dissertation Abstr.*, **26**, 4247 (1966).

(10) R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 259–276.

(11) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

(12) M. Vogel and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 2262 (1966); M. E. Hawden and J. D. Roberts, *Tetrahedron Suppl.*, **2**, 403 (1963); R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, 81, 4390 (1959), and references therein cited.

(13) P. von R. Schleyer and G. W. van Dine, *ibid.*, **88**, 2321 (1966), and references therein cited.

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(16) J. L. von Rosenberg, Jr., J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962); S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965); C. E. Keller and R. Pettit, *ibid.*, **88**, 604, 606 (1966); S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966). The last authors estimate that the homotropylium is 22.3 kcal/mole more stable than a planar cyclooctatrienyl cation.

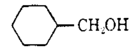
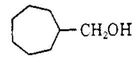
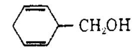
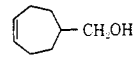
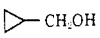
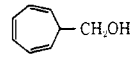
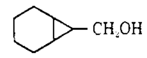
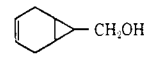
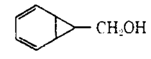
(17) Reviews: A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 277–279; T. Nozoe in "Non-Benzenoid Aromatic Compunds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 7.

(18) A review: G. Maier, *Angew. Chem. Intern. Ed. Engl.*, **6**, 402 (1967).

(19) W. von E. Doring and D. W. Wiley, *Tetrahedron*, 11, 138 (1960). The experimental difficulties arose during preparation of 7-carboxymethylcycloheptatriene by irradiation of methyl diazoacetate in benzene. No conditions could be found to prevent simultaneous production of isomeric carboxymethylcycloheptatrienes and methyl phenylacetate. The generation of these contaminants occurs to some extent during the photolysis, but is more pronounced during subsequent work-up.

(20) H. J. Dauben, Jr., personal communication. We are grateful to Professor Dauben for furnishing us with details of this procedure prior to publication.

Table I. Solvolytic Reactivity of Derivatives of Selected Alcohols

	k_1, sec^{-1}			
Parent alcohol (ROH)	ROBs,[a] acetic acid 80°	ROTs,[a] acetic acid 30°	RODNB,[d] 60% aq acetone 100°	Rel react.
	1.50×10^{-6} [b]			0.012
 VII	6.60×10^{-6} [c]			0.051
 VIII	1.29×10^{-4} [d]	7.2×10^{-8} [e]		1.0
 IX	4.05×10^{-4} [c]			3.1
		3.38×10^{-4} [f]	4.30×10^{-7} [g]	4,700
 I			2.6×10^{-6}	28,000
 X			9.65×10^{-5} [g]	1.1×10^6
			*Ca.* 1.5×10^{-5} [h]	1.6×10^5
 IV			(2.6×10^{-2})[i]	2.8×10^8

[a] ROBs = *p*-bromobenzenesulfonate; ROTs = *p*-toluenesulfonate; RODNB = 3,5-dinitrobenzoate. [b] In the presence of 0.0478 *M* potassium acetate.[15] [c] In the presence of 0.0435 *M* potassium acetate.[15] [d] Calculated from ROTs rates at 82.8 and 70.0°[14] by interpolation and by assuming that ROBs solvolyzes three times more rapidly than ROTs. [e] Extrapolated from rates at higher temperatures.[14] [f] D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964). [g] Reference 13. [h] G. D. Sargent and N. Lowry, unpublished results. [i] Estimated, see text.

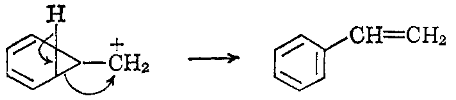
carbinol (VII)! That this enhanced rate does not result from prior isomerization of Ib to an allylic ester is shown by the fact that unreacted dinitrobenzoate recovered after exposure to solvolytic conditions for one half-life was found to be identical with Ib (infrared, nmr, melting point, mixture melting point).

Solvolysis of Ib conducted for several half-lives in the presence of excess urea, a nonnucleophilic base added to sequester 3,5-dinitrobenzoic acid as it is formed, yields only two products, Ia (73 ± 6% absolute yield) and styrene. Since Ia was shown to be stable under the conditions of product formation and characterization, styrene must be a primary product of the solvolysis reaction.

The solvolytic reactivity of I is enhanced by factors of 2.8×10^4 and 9×10^3 relative to the model compounds 6-hydroxymethyl-1,4-cyclohexadiene (VIII) and 5-hydroxymethylcycloheptene (IX), respectively (Table I). Coupled with the nature of the observed products, this observation[21] serves to rule out processes 1 and 2 as the source of transition-state stabilization in the solvolysis of Ib.

Both the high yield of unrearranged product and the formation of styrene as a primary solvolysis product are inconsistent with C_1–C_7 σ-electron participation (process 3). In addition, the product most likely to result from intervention of the homotropylium ion, cyclooctatetraene,[16] was not found to be present in the product mixture from solvolysis of Ib, even though as little as 0.5% could have been detected. Since hydride participation (process 4) would undoubtedly proceed irreversibly, the nature of the observed solvolysis products serves to exclude this, too, as the source of the high solvolytic reactivity shown by Ib.

We are thus forced to the conclusion that solvolysis of Ib involves prior isomerization to the valence tautomer IV. Participation by cyclopropane in the solvolysis of IV readily accounts for both the accelerated reaction rate and the formation of unrearranged product in high yield. The cyclopropyl carbonium ion derived from IV can also serve as the immediate precursor for the only other observed product, styrene, which would arise directly by deprotonation with concomitant fragmentation of the cyclopropane ring. To our knowledge, this



represents the first report of a solvolysis reaction preceded and initiated by valence tautomerism.

Although the cycloheptatriene–norcaradiene interconversion has been widely postulated to be a mobile equilibrium,[18] the presence of the norcaradiene tautomer has never been detected directly either in cycloheptatriene itself or in any singly substituted cyclo-

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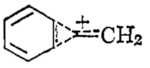
[21] This argument tacitly assumes that the nucleophilicity of conjugated double bonds does not markedly exceed that of isolated double bonds. Support for this assumption is found in the observation that remote double bond participation accelerates the solvolysis of 2-(7-cycloheptatrienyl)ethyl *p*-nitrobenzenesulfonate by only a factor of 20: unpublished research with T. E. McLaughlin.

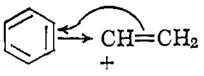
heptatriene. Rather, its presence has been inferred from the existence of reactions of cycloheptatriene which generate products logically derived from norcaradiene. In no previous case, however, have these reactions rationally *required* the prior formation of norcaradiene. In the present instance, by contrast, the kinetic results can only be explained by invoking in the transition state for ionization the full electron-donating capability associated with preformed cyclopropane rings.

The observed solvolysis rate constant for Ib actually underestimates the solvolytic reactivity of IV. From the observed free energy of activation for solvolysis of Ib must be subtracted the free energy difference between Ib and the less stable IV, in order to obtain the actual free energy of activation for solvolysis of IV. Since the nmr spectrum ($CDCl_3$) of Ib shows no trace of IV, this free energy difference must be at least 2.5 kcal/mole. It is more likely in the range 6–14 kcal/mole.[22] By assuming the *minimum* value of this range, one calculates that the true rate constant for solvolysis of IV (100°) is 2.6×10^{-2} sec^{-1}, a value more than two powers of ten greater than that for the most reactive dialkyl-substituted cyclopropylcarbinyl dinitrobenzoate previously reported.

The basis for this enhanced reactivity is as yet undefined, but it is interesting to note that recent formulations of the cyclopropyl carbonium ion impute some double bond character to the bond joining the two carbon atoms β to the site of ionization. In the present instance, such a formulation (XI[13] or XII[3]) imparts partial benzenoid character to the norcaradiene six-membered ring.



XI



XII

Acknowledgment. We are grateful to the National Science Foundation and to the donors of the Petroleum Research Fund administered by the American Chemical Society for financial support.

[22] The dilatometric technique which was able to detect 0.01% bicyclic valence tautomer in cyclooctatetraene failed to detect norcaradiene in cycloheptatriene [R. Huisgen, *Angew. Chem.*, 76, 928 (1964)]. By utilizing standard bond energies, Doering and Willcott estimate that norcaradiene is less stable than cycloheptatriene by 11–14 kcal/mole: W. von E. Doering and M. R. Willcott, III, unpublished calculations; M. R. Willcott, Ph.D. Thesis, Yale University, 1963.

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Received July 24, 1967

Oxygen Isotopic Fractionation in the Reduction of Aquotetraamminechromium(III). Evidence for a *trans* Effect

Sir:

It has been suggested by a number of authors that the rearrangement of bonds to nonbridging ligands may be an important part of the activation process for some inner-sphere redox reactions.[1,2] Very recently Pennington and Haim[3] suggested that the large difference in the rates of reactions of the *cis* and *trans* isomers of some bis(ethylenediamine)chromium(III) complexes with chromium(II) could be explained by assuming that the bond to the ligand *trans* to the bridging group had to be stretched to make the activated complex. Several years ago, Taube and co-workers[2,4] began seeking direct experimental evidence for such bond rearrangements in the form of isotopic fractionation measurements. Green, Schug, and Taube[4] measured nitrogen isotopic fractionation factors for the reactions of a number of cobalt(III)–ammine complexes with aquochromium(II) ion and concluded that stretching of cobalt–nitrogen bonds was not important in the reactions studied. Their results are not surprising in retrospect, in view of the small difference in bond distances between cobalt(II) and cobalt(III) ammines.[5] A more substantial difference in geometry exists between the complexes of chromium(II) and chromium(III) with weak field ligands,[6] and it seemed to us that measurements of isotopic fractionation for atoms bound to chromium(III) would constitute a more meaningful test of the bond-stretching hypothesis.

We have measured the fractionation of O^{16} compared to O^{18} in the reaction of *trans*-chloroaquotetraamminechromium(III) ion with aquochromium(II) ion. The reaction under study is actually the chromium(II)-catalyzed loss of ammonia from the chromium(III) complex, the main net change being described by

$$(NH_3)_4Cr(OH_2)Cl^{2+} + 4H_3O^+ \longrightarrow 5NH_4^+ + (H_2O)_5CrCl^{2+} \quad (1)$$

It is generally accepted that the catalysis of such reactions by chromium(II) involves an electron-transfer reaction as the rate-determining step.[1,2] That net replacement of chloride is not observed is taken to be evidence that the redox reaction is of the inner-sphere type.

The salt *trans*-$[Cr(NH_3)_4(OH_2)Cl](ClO_4)_2$ was mixed with $Cr(ClO_4)_2$ in *ca.* 2 *M* $HClO_4$ and allowed to react for two or more half-times. The reaction was quenched, and the unreacted *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ was retrieved. The ratio $[O^{18}]/[O^{16}]$ was determined for the *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ before reaction and for the complex retrieved from the reaction mixture. It was found that the $[O^{18}]/[O^{16}]$ ratio increased steadily with the extent of reaction. From these ratios we calculate that the kinetic isotopic fraction factor $(d \ln [O^{16}])/(d \ln [O^{18}]) = k_{O^{16}}/k_{O^{18}} = 1.016 \pm 0.001$, where $k_{O^{16}}$ and $k_{O^{18}}$ represent the rate constants for ions of the complex containing O^{16} and O^{18}, respectively.

Preliminary data have also been obtained for the reaction of *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ with Cr^{2+}, and these allow an upper limit to be set for the fractionation factor for the *cis* complex, namely, $k_{O^{16}}/k_{O^{18}} \leqq 1.007$.

The isotope fractionation data indicate that *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ reacts with Cr^{2+} 1.6% faster when the water molecule *trans* to the bridge contains O^{16} than when the water molecule contains O^{18}. Thus a substantial stretching of the bond to the *trans* ligand

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