sketched for the purpose of indicating roughly how the various quantities of interest (charge distribution and energy) are related. Then, rather than to actually use the L.C.A.O. theory, estimating the values of the integrals used by semi-empirical considerations, we abandon thought of any attempt to actually use the theory for numerical calculations, but develop a parallel theory in terms of quantities more directly related to experiment, such as bond polarizabilities. The not-unexpected result is that we end up with more accurate correlations of bond energies, activation energies, bond polarizabilities and dipole moments, than previously was possible, as is evidenced by our results.

The reason for the linearity represented in Figs. 1 and 2 is, similarly, not to be sought for in the L.C.A.O. equations, but in the closer-to-experiment model which actually is used. It is most conveniently discussed in terms of what might be called the "Principle of Linear Superposition of Small Resonance Effects." The processes we have discussed all involve creating what we have called a "hole," *i.e.*, a place where electrons from the various parts of a molecule can spend a small fraction of their time, resulting in a lowering of the electronic energy. Removing a hydrogen from a hydrocarbon, for example, will produce a "hole" of a certain depth. Substituting a hydrogen by a chlorine will produce a less deep hole. How much good will be gained from the formation of the hole will be, essentially, the product of two factors—a capacity factor (σ) and an intensity factor (ρ). The σ factor has to do with how many electrons are available from a given molecule to make use of the hole, so that there will be a particular σ for methyl, one for ethyl, and so on. The intensity factor (ρ) has to do with the "depth of the hole"—that is, how much good an electron gains from the use of the extra available space. Substituting a hydrogen by chlorine results in a particular ρ; bromine gives another ρ, and so on. Now when the resonance effects are small, the ρ and σ factors will be independent, for an electron will make use of the extra available space for such a short time that it will not interfere with other electrons using the space—that is, small resonance effects are superposed, the interference of the effects is negligible, so that the capacity and intensity factors will be independent. The σ and ρ discussed above obviously are related to Hammett's σ and ρ constants for substituted benzenes, and the same explanation applies there. It is planned to discuss the σ–ρ correlation more extensively in a future paper of this series.

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[CONTRIBUTION NO. 252 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE][1]

The Kinetics of the Cerium(IV)-Chloride Reaction. The Cerium(IV)-Thallous Reaction in the Presence of Chloride

BY FREDERICK R. DUKE AND CURTIS E. BORCHERS

RECEIVED MAY 27, 1953

The oxidation of chloride by Ce(IV) proceeds through the disproportionation of $CeCl_2^{+2}$, $CeCl_3^{+}$ and higher chloride complexes. Thallous ion is not attacked by Ce(IV) in perchlorate solutions and is not directly attacked when Cl^- is present. Thus, Tl(I) was added to reaction mixtures to maintain a constant Cl^- concentration and to prevent the formation of mixtures of oxidation products of Cl^-. The hydrolyzed form of cerium, $Ce(OH)^{+3}$, does not appear to react with chloride.

Introduction

The oxidation of chloride ion by cerium(IV) proceeds chiefly to the production of chlorine. However, at low chloride concentrations, a large amount of higher oxidation states of chlorine is formed in the reaction, making kinetic study difficult if not impossible. However, upon addition of $TlClO_4$, the first oxidation product of the chlorine appears to be reduced back to chloride with no complications, the over-all reaction being zero order in Tl(I).[2] Thus, conditions were found which allowed the kinetic study to proceed with interpretable data.

Experimental

Sulfate-free ceric perchlorate was prepared by electrolysis of purified cerous perchlorate. This was standardized against sodium oxalate. $LiClO_4$ was prepared by dissolving lithium metal in water and neutralizing with perchloric acid. The $LiClO_4$ was standardized by acid–resin exchange and titration of the acid. $TlClO_4$ was prepared by dissolving thallium metal in dilute perchloric acid and concentrating to precipitate the salt. This was filtered, washed with water, dissolved and standardized by the method of Willard and Young.[3] Reagent grade HCl, $HClO_4$ and H_2SO_4 were used and standardized with Na_2CO_3.

Each rate run was made in the following general manner: appropriate amounts of $HClO_4$, HCl, $LiClO_4$ and $TlClO_4$ were pipetted into a 50-ml. aluminum-foil covered flask and diluted to 49 ml. The flask was placed in a 25 ± 0.1° water-bath for half an hour, the ceric perchlorate added, and the flask filled to 50 ml. An electric timer was started as the ceric solution passed into the flask. Five-ml. aliquots were withdrawn at timed intervals and quenched in 5 ml. of approximately 6 *M* sulfuric acid. The time was taken as the meniscus passed a mark on the pipet. The absorbency of these quenched solutions was measured with a Coleman Jr. spectrophotometer at 420 mμ. The Ce(IV) concentration was then obtained from a calibration curve. This calibration curve was obtained by measuring the absorbency of 5 ml. of known concentrations of Ce(IV) and perchloric acid in 5 ml. of sulfuric acid. The absorbency of any one quenched aliquot did not change for as long a period as 48 hours.

Results and Discussion

Each rate run was repeated at least once and in some cases twice. When the log Ce(IV) concentra-

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] (a) A. E. Remick, THIS JOURNAL, **69**, 94 (1947); (b) P. A. Schaffer, *ibid.*, **55**, 2169 (1933).

[3] H. H. Willard and P. Young, *ibid.*, **52**, 36 (1930).

tion was plotted against the time, straight lines were obtained. Most of the points fell along this line within experimental error; the exceptions were the runs where the Cl^- to Ce(IV) concentration ratio was small.

In these cases the first-order plot curved, the first-order "constant" decreasing with time. Comparison of the initial slopes where only the initial Ce(IV) concentration was changed, indicated that the initial slopes of the first-order plots were independent of the Ce(IV) concentration; that is, the reaction remains first order in Ce(IV) at low $[Cl^-]$. These results also show that Ce(IV) does not form a kinetically detectable amount of chloride complex at these low chloride concentrations. On the other hand, the Tl(III), the ultimate product of the reaction, forms very stable $TlCl^{+2}$ and $TlCl_2^+$ complexes,[4] and at low $[Cl^-]$ an appreciable percentage of the chloride present may become bound in these complexes before the reaction is completed. The curvature of the first-order plots at low $[Cl^-]$ is quantitatively explained in this manner if it is assumed that the reaction is second order in chloride ion. The results listed below indicate that this order at low $[Cl^-]$ is correct. In Table I first-order pseudo-constants obtained from log Ce(IV) *vs.* time plots are tabulated with various concentrations of Ce(IV), Tl^+, H^+ and Cl^-. In all runs the ionic strength was 4. The pseudo-constant may be a function of $[Cl^-]$, $[H^+]$ and [Tl(I)].

The first group of runs shows that the rate is independent of the Tl(I) concentration. The rate expression thus becomes

$$\frac{-d[Ce]}{dt} = k_I\,[Ce] \times F([H^+]) \times F([Cl])$$

where k_I is the specific rate constant for the reaction.

TABLE I

FIRST-ORDER PSEUDO-CONSTANTS

[Ce(IV)]	$[H^+]$	$[Cl^-]$	[Tl(I)][a]	k'
0.001	4.00	0.005	0.001	4.14×10^{-5}
.001	4.00	.005	.002	4.14×10^{-5}
.001	4.00	.005	.004	3.85×10^{-5}
.002	4.00	.005	.002	4.22×10^{-5}[b]
.002	4.00	.01	.002	1.26×10^{-4}
.002	4.00	.02	.002	6.43×10^{-4}
.002	4.00	.04	.002	2.90×10^{-3}
.002	3.00	.04	.002	2.51×10^{-3}
.002	2.00	.04	.002	2.07×10^{-3}
.002	1.00	.04	.002	1.00×10^{-3}

[a] Expressed as normality. The others are molarities.
[b] Initial slope.

The second group of runs gives the dependence of the reaction upon the chloride ion concentration. As the reaction is independent of Tl^+ the rate determining step must be the reaction between Cl^- and Ce(IV) to form Ce(III) and oxidation product of Cl^-. If one assumes complex formation between the Ce(IV) and the Cl^-, with the other initial ion concentrations held constant, the general rate expression is[5]

$$\frac{-d[Ce]}{dt} = k_0[Ce] + k_1[CeCl^{+3}] + k_2[CeCl_2^{+2}] + \cdots\cdots k_n[CeCl_n^{-(n+4)}]$$

where the small k's represent rate constants. If

$$Ce^{+4} + Cl^- \rightleftarrows CeCl^{+3} \quad K_1 = \frac{[CeCl^{+3}]}{[Ce^{+4}][Cl^-]}$$

$$CeCl^{+3} + Cl^- \rightleftarrows CeCl_2^{+2} \quad K_2 = \frac{[CeCl_2^{+2}]}{[CeCl^{+3}][Cl^-]}$$

$$CeCl^-{}_{n-1}{}^{(n-3)} + Cl^- \rightleftarrows CeCl_n^{-(n-4)}$$

$$K_n = \frac{[CeCl_n^{-(n-4)}]}{[CeCl_{n-1}^{-(n-3)}][Cl^-]}$$

and

$$T_{Ce} = Ce^{+4} + CeCl^{+3} + CeCl_2^{+2} + \ldots\ldots CeCl_n^{-(n-4)}$$

the rate expression becomes

$$\frac{-[T_{Ce}]}{dt} = \left[\frac{k_0 + k_1K_1[Cl^-] + k_2K_1K_2[Cl^-]^2 + k_3K_1K_2K_3[Cl^-]^3 + \ldots\ldots}{1 + K_1[Cl^-] + K_1K_2[Cl^-]^2 + K_1K_2K_3[Cl^-]^3 + \ldots\ldots}\right][T_{Ce}]$$

and k' is the bracketed portion of the rate expression. At low $[Cl^-]$ the denominator may be assumed to be unity and the constants may be estimated graphically. A plot of k' *versus* $[Cl^-]$ and k'/Cl^- *versus* $[Cl^-]$ give zero intercepts. This shows that Ce(IV) and $CeCl^{+3}$ do not proceed to end products. A plot of $k'/(Cl^-)^2$ *versus* $[Cl^-]$ gives a small positive intercept, I. A plot of $(k'/[Cl^-]^2 - I)/[Cl^-]$ has a negative slope; this indicates that the denominator of the rate equation has become appreciable at the higher $[Cl^-]$ and can no longer be assumed to be one. This result justifies the assumption that cerium(IV)–chloride complexes are involved. Attempts to evaluate the equilibrium constants, assuming $CeCl_3^+$ to be the highest complex formed, yield unsatisfactory values; thus, higher complexes than $CeCl_3^+$ are being formed and cannot be neglected in the approximations necessary to evaluate the constants. Since the slope of the plots are combinations of numerator and denominator effects, the equilibrium and rate constants cannot be separated.

The third group of runs shows the effect of the H^+ on the reaction. Assuming the effect of the H^+ is entirely due to the equilibrium

$$Ce(H_2O)_n{}^{+4} \rightleftarrows Ce(H_2O)_{n-1}OH^{+3} + H^+$$

then

$$K_D = \frac{[T_{Ce}{}^{+4} - Ce^{+4}][H^+]}{[Ce^{+4}]}$$

and

$$Ce^{+4} = \frac{[T_{Ce}][H^+]}{[H^+] + K_D}$$

Substituting this in the rate equation

$$\frac{-d[T_{Ce}]}{dt} = k''[T_{Ce}]F([H^+])$$

where k'' includes the function of the chloride ion, as its initial concentration is constant for this series of runs; the rate equation becomes

$$\frac{-d[T_{Ce}]}{dt} = \frac{k''[H^+]}{[H^+] + K_D}[T_{Ce}]$$

The pseudo-rate constant is then

$$k' = \frac{k''[H^+]}{[H^+] + K_D}$$

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[4] R. Benoit, *Bull. soc. chim. France*, **518** (1949).

[5] See, for example, F. R. Duke and R. F. Bremer, THIS JOURNAL, **73**, 5179 (1951).

and inverting

$$\frac{1}{k'} = \frac{1}{k''} + \frac{K_D}{[H^+]k''}$$

is obtained. Hardwick and Robertson[6] have obtained an equilibrium constant of 5.2 for the dissociation reaction in 2 *M* perchloric acid at 25°. Using their value with our data, satisfactory slope and intercept are obtained for a $1/k'$ *versus* $1/[H^+]$ plot.

The most probable first product in the reaction is probably the free radical ion, Cl_2^-. This ion apparently has sufficiently lower free energy than the Cl atom that it may be formed, and Cl atoms may not be formed. This reaction may be

$$CeCl^{+3} + Cl^- \longrightarrow Ce^{+3} + Cl_2^-$$

or a complex of the form $CeCl_2^{+2}$ may be formed before formation of the products. The ion Cl_2^- and similar ions have been found as intermediates in previous work.[7]

AMES, IOWA

[6] T. Hardwick and Robertson, *Canadian J. Chem.*, **29**, 818 (1951).

[7] H. Taube and W. Bray, THIS JOURNAL, **62**, 3357 (1940); H. Taube, *ibid.*, **69**, 1418 (1947); *ibid.*, **70**, 3928 (1948).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

Molecular Addition Compounds of Dinitrogen Tetroxide. III.[1,2] Binary Systems with a Series of Aliphatic and Alicyclic Mono-, Di- and Tribasic Ethers

BY JEAN GUTHRIE WHANGER[3] AND HARRY H. SISLER

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The binary systems formed by dinitrogen tetroxide with the following ethers have been studied by the freezing point method: *n*-propyl ether, *n*-butyl ether, isopropyl ether, *t*-butyl ether, ethylene glycol diethyl ether, 1,3-dioxane, trioxane, perfluorotetrahydrofuran and α-methyltetrahydrofuran. Compounds of the type $N_2O_4 \cdot 2B$ are formed with α-methyltetrahydropyran and ethylene glycol diethyl ether, and probably with *n*-propyl ether, isopropyl ether, *n*-butyl ether though in these cases incongruent melting points obscure the maxima in the freezing point curves. Compounds of the type $N_2O_4 \cdot B$ were obtained with 1,3-dioxane, ethylene glycol diethyl ether and probably with trioxane. No compounds of dinitrogen tetroxide, with *t*-butyl ether and perfluorotetrahydrofuran were indicated by these studies. Theoretical implications of these results are briefly discussed.

Introduction

In a recent publication[1] from this Laboratory, one of the authors and his co-workers showed that dinitrogen tetroxide combines with several aliphatic and alicyclic ethers to form molecular addition compounds of the type $N_2O_4 \cdot 2B$ where B is one molecule of the ether. In a few instances, compounds of the formula $N_2O_4 \cdot B$ are obtained. Magnetic and spectroscopic studies reported at that time indicated that these compounds are true addition compounds of the N_2O_4 molecule and do not contain NO_2 radicals or NO^+, NO_3^-, NO_2^+ or NO_2^- ions.

In an effort to obtain information concerning the various parameters which limit the field of application of this reaction and perhaps thereby to establish certain implications concerning the structures of these dinitrogen tetroxide–ether addition compounds, the binary systems of dinitrogen tetroxide with the following additional ethers were studied: *n*-propyl ether, isopropyl ether, *n*-butyl ether, *t*-butyl ether, 1,3-dioxane, trioxane, ethylene glycol diethyl ether, perfluorotetrahydrofuran and α-methyltetrahydrofuran. The assistance of the Ordnance Corps, U. S. Army, through a contract with The Ohio State University Research Foundation in carrying out this research is gratefully acknowledged.

Experimental

Preparation of Materials.—The preparation and purification of dinitrogen tetroxide has been discussed in the previous publication in this series.[1] The ethers were all prepared or purified and stored according to accepted procedures. Physical constants for the purified samples used are listed in Table I along with comparable data from the literature for comparison. It should be noted that tendency to glass formation prevented our obtaining good freezing points for α-methyltetrahydrofuran and perfluorotetrahydrofuran.

TABLE I

PHYSICAL CONSTANTS OF ETHERS

Ethers	Boiling points, °C. Exptl.	Lit.	Freezing points, °C. Exptl.	Lit.
n-Propyl[a]	89.5 (751 mm.)		−122	−122.5
Isopropyl[a]	68.3 (754 mm.)		−85	−85.89
n-Butyl[a]			−95	−95.37
Ethylene glycol–diethyl[a]			−73	−74
Tertiary butyl[b]			−60	−60
1,3-Dioxane			−42.7	−42
Trioxane[c]			63 to 64	63 to 64
α-Methyltetrahydrofuran[d]	80	80	Forms glass	
Perfluorotetrahydrofuran[e]			Forms glass	

[a] Eastman Kodak Company. [b] Furnished by the American Petroleum Institute at The Ohio State University. [c] Heyden Chemical Corporation. [d] Furnished by Christopher E. Wilson, Ohio State University. [e] Furnished by Minnesota Mining and Manufacturing Company.

Procedure.—The freezing point–composition diagrams for the binary systems composed of dinitrogen tetroxide with each of the various ethers were determined by methods described in the previous publication in this series.[1] Briefly the freezing points of synthetic mixtures were determined by cooling curves measured by a Micromax self-recording potentiometer with a copper–constantan thermocouple, using a completely enclosed cell equipped for continuous magnetic stirring. In those instances where a slow oxidation-reduction reaction between dinitrogen tetroxide and the ether occurs (*t*-butyl ether and α-methyltetrahydrofuran) the effects of this reaction were minimized by not warming the mixtures any higher than necessary and by frequently taking fresh samples. However, in these instances, somewhat less than usual accuracy must be ascribed to the results.

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[1] The first paper in this series: B. Rubin, H. Sisler and H. Shechter, THIS JOURNAL, **74**, 877 (1952).

[2] The second paper in this series: D. Davenport, H. Burkhardt and H. Sisler, THIS JOURNAL, **75**, 4175 (1953).

[3] Taken in part from the dissertation submitted by J. G. W. in partial fulfillment of the requirements for the Ph.D. degree at The Ohio State University.