0–2 indicate $E_B{}^0$ and E^0 for the Ga(I)–Ga(III) couple are ≥ 1.24 and $\sim\geq 0.40$ v., respectively.

Experimental

The cell for kinetic studies was made from a 40/50 standard taper joint sealed at both ends. The internal stirrer consisted of a glass rod with a bar magnet sealed crosswise near the top and glass stirring blades fused on near the bottom, and was mounted between a dimple in the cell top and the narrow opening of a capillary stopcock in the bottom piece. With Ga_2Cl_4 in the evacuated cell, solvent was admitted through the bottom stopcock, the apparatus pressurized with N_2 previously equilibrated with the solvent, and then opened to a gas buret. The H_2 evolution was measured at constant pressure to ±0.01 ml. for one to four half-lives and corrected for the vapor pressure of the solution. The final reducing strength C_t was determined by addition of standard I_3^- solution to an aliquot, acidification, and back titration. In the few cases where C_t was uncertain, the rate was evaluated independent of this from plots of C' *vs.* the graphically derived dC'/dt. Since impurities in commercial $NaClO_4$ were found to react with iodine solutions, this was prepared from reagent grade NaOH and $HClO_4$, and its concentration determined by titration before and after exchange of the solution with Dowex-50 in the acid cycle.

CONTRIBUTION FROM THE MAX-PLANCK-INSTITUT FÜR
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Second Wien Effect in Aqueous Mercuric Chloride Solution[1]

BY MANFRED EIGEN AND EDWARD M. EYRING

Received August 13, 1962

Onsager[2] suggested in his classic treatment of the second Wien effect[3] that the equilibrium

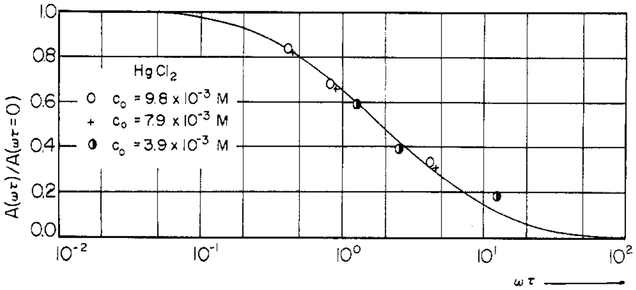

Fig. 1.—Experimental dispersions of the field effect in aqueous mercuric chloride solutions. Each set of three points corresponds to the three different pulse lengths (frequencies) $\omega_1 = 4 \times 10^5$ sec.$^{-1}$, $\omega_2 = 8 \times 10^5$ sec.$^{-1}$, and $\omega_3 = 3.8 \times 10^6$ sec.$^{-1}$ reading from left to right.

$$HgCl_2 \underset{k_R}{\overset{k_D}{\rightleftharpoons}} HgCl^+ + Cl^- \qquad (1)$$

would make a particularly interesting experimental rate study because of the hydrodynamic effect of the large cation on the specific rate k_R of the recombination reaction. Bailey and Patterson[4] subsequently measured a fractional increase in high field conductance of about 1.7% for an aqueous 9.3×10^{-3} *M* solution of $HgCl_2$ at 25° as the field was increased from 40 to 100 kv./cm. They tentatively attributed the observed effect to reaction 1 but could not exclude the possibility that hydrolysis plays a significant role.

For $HgCl_2$ solutions of similar concentrations we have obtained extrapolated values of $\Delta\Lambda/\Lambda_0$ (Table I) of about the same size as those noted by Bailey and Patterson. Our technique[5] though less suitable than Patterson's instrument for making absolute Wien effect measurements, also permits the determination of a relaxation time τ, which for a simple dissociation equilibrium according to eq. 1 would read

$$\tau = (k_D + 2k_R x_e)^{-1} \qquad (2)$$

The symbol x_e in eq. 2 denotes the equilibrium concentration of one of the reacting ionic species which is assumed to be equal for Cl^- and $HgCl^+$. Even if the equilibrium constant K is not known, it frequently is possible to determine both the specific rate for dis-

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[1] Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J. September, 1962.

[2] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

[3] M. Wien and J. Schiele, *Z. Physik*, **32**, 545 (1931). The second Wien effect or dissociation field effect is a marked, non-ohmic increase in the electrical conductance of a solution of a weak electrolyte when a high intensity electric field is applied. Effectively, the field displaces the equilibrium

$$\text{molecules} \rightleftharpoons \text{ion pairs} \rightleftharpoons \text{free ions}$$

to the right by pulling apart some of the ion pairs. In the range 40 to 100 kv./cm. the increase in conductance for a weak electrolyte will be proportional to the absolute value of the field intensity and, depending on concentration, can be as large as 10% of the conductance in the absence of a strong field. Earlier (1927) Wien reported a first Wien effect in solutions of both strong and weak electrolytes. This more modest increase in electrical conductance with increasing field gradient arises primarily from the destruction of the ionic atmosphere by the high field with a consequent increase in ion mobility. We denote the absolute change of equivalent conductance arising from both Wien effects by $\Delta\Lambda/\Lambda_0 = (\Lambda_X - \Lambda_0)/\Lambda_0$, where Λ_X is the equivalent conductance of the solution at field x and Λ_0 is the equivalent conductance of the same solution at zero field. Since our experimental comparison system cancels most of the ion atmosphere effect in our mercuric chloride solutions, our observed $\Delta\Lambda/\Lambda_0$ is presumed to arise solely from a second Wien effect. Onsager[2] quantitatively described the second Wien effect by the equation

$$\Delta\Lambda/\Lambda_0 = [(1 - \alpha)/(2 - \alpha)]b\Delta E$$

where $\alpha = ci/c_0$ is the degree of dissociation, ci is the concentration of each of the recombining ions, c_0 is the total solute concentration, E is the electric field intensity, and b is a known function of ion mobilities, ion charge, solvent dielectric constant, and temperature.

[4] F. E. Bailey, Jr., and A. Patterson, Jr., *J. Am. Chem. Soc.*, **74**, 5759 (1952).

[5] M. Eigen and J. Schoen, *Z. Elektrochem.*, **59**, 483 (1955). We apply a high voltage pulse having the form of a critically damped, harmonic oscillation across a balanced, symmetric, bifilar-concentric bridge. The sample and reference cells are identical (2.0-mm. electrode distance, cell constant 0.053 cm.$^{-1}$). In the reference cell there is a dilute aqueous solution of HCl to cancel the first Wien effect in the sample cell. The remaining two arms of the bridge are cells with considerably greater electrode distances containing aqueous NaCl. The field intensity in these cells never exceeds a few kv./cm. The bridge and an auxiliary Wagner grounding circuit are the damping resistance in an RLC resonant circuit. We use half-wave, high voltage pulses of three different lengths: 2.5, 1.25, and 0.26 μsec. In a determination of the relaxation time τ of the mercuric chloride equilibrium for a given concentration of the salt in the sample cell we begin by applying a series of 1.25 μsec. pulses of increasing voltage to the bridge. The bridge is balanced oscillographically, and from the measured conductance at each voltage we plot the linear dependence of $\Delta\Lambda/\Lambda_0$ on $|E|$ over the range E = 40 to 100 kv./cm. Similar straight line plots are obtained with the 0.26 and 2.5 μsec. pulses. In case of a relaxation process these three straight lines are not superimposed; such a dispersion of the second Wien effect is shown in Fig. 1. The ordinate $A(\omega\tau)/A\cdot(\omega\tau = 0)$ is a reduced amplitude of the conductivity change during the sinusoidal high voltage pulse, and the ω in the abscissa $\omega\tau$ is the reciprocal of the duration of the critically damped harmonic oscillation, *i.e.*, the circular frequency in sec.$^{-1}$.

TABLE I

DISSOCIATION FIELD EFFECT DATA FOR AQUEOUS SOLUTIONS OF MERCURIC CHLORIDE AT 24–25°

c_0, mole/l.	$\Delta\Lambda/\Lambda_0$ (E = 40 to 100 kv./cm.)	[H$^+$], mole/l.	τ, μsec.	Sample conductivity, 10^{-6} ohm^{-1}-cm.$^{-1}$
9.8×10^{-3}	3%	7.6×10^{-5}	0.95 ± 10%	48 ± 1
7.9×10^{-3}	2%	7.9×10^{-5}	1.02 ± 10%	47 ± 1
3.9×10^{-3}	2%	3.2×10^{-5}	2.9 ± 30%	38 ± 1

sociation and that for recombination, k_D and k_R respectively, as well as K, by determining τ for several different ion concentrations and using eq. 2 with the relation $K = k_D/k_R$. In Table I we present experimental data obtained by the dissociation field effect method[5] for three different aqueous $HgCl_2$ solutions. In the last column we have the sample conductivity in (ohm-cm.)$^{-1}$. The sample solutions were prepared from analytical grade $HgCl_2$ (manufactured by E. Merck, Darmstadt, m.p. 276°) and water, distilled in quartz under a nitrogen atmosphere, that had a conductivity not greater than 2×10^{-7} ohm^{-1} cm.$^{-1}$. The concentrations were low enough so that the solubility products of $HgCl_2$ and $Hg(OH)_2$ were not exceeded. The measured conductivity of the $HgCl_2$ solutions agreed well with values reported by Joshi and Solanki.[6] The longest high field pulse had a duration of only 1 μsec., so that differential heating effects between the sample and hydrochloric acid reference solutions could be ignored.[4] It was not possible to determine τ with this instrument for a wider range of $HgCl_2$ concentrations: the Wheatstone bridge could not be balanced for higher concentrations, and at lower concentrations the Wien effect was too small for reliable measurements and showed insufficient dispersion for satisfactory interpretation.

Since the equilibrium responsible for the second Wien effect cannot be identified directly, the concentrations of all species in solution were examined for likely candidates. The concentrations of the important species can be estimated from the relations

$$[HgOH^+]^2/[Hg(OH)_2][Hg^{+2}] = 0.08 \qquad (3)^{7}$$

$$[Hg^{+2}][Cl^-]/[HgCl^+] = 10^{-6.74} \qquad (4)^{8}$$

$$[Hg^{+2}][Cl^-]^2/[HgCl_2] = 10^{-13.22} \qquad (5)^{8}$$

$$[H^+] = [HgOHCl] + 2[Hg(OH)_2] + [HgOH^+] \qquad (6)^{9}$$

$$C_0 \approx [HgCl_2] + [HgCl^+] + [HgOHCl] \qquad (7)^{10}$$

$$[Cl^-] = 2C_0 - [HgCl^+] - 2[HgCl_2] - [HgOHCl] \qquad (8)^{11}$$

The equilibrium constants for (3) through (5) are for 0.5 M ionic strength. Since our solutions had ionic strengths near 10^{-4} M, we would prefer to use the "thermodynamic" equilibrium constants. Anderegg, *et al.*,[12] obtained a thermodynamic equilibrium constant of 0.04 for (3) by extrapolating to infinite dilution. Sillén[8] has shown that thermodynamic equilibrium constants for (4) and (5) can be estimated from known activity coefficients of related mercurous compounds and HgI_2. Another set of thermodynamic equilibrium constants for aqueous $HgCl_2$ solutions proposed by Damm and Weiss[13] is unsuitable since $Hg(OH)_2$ was omitted and $HgOH^+$ was included in spite of the fact that the latter is present in much smaller concentrations for all pH values greater than unity.[7,12] Since in dilute aqueous $HgCl_2$ solutions the ions $HgCl_3^-$ and $HgCl_4^{-2}$ are present in negligible concentrations,[8] we have omitted these species from consideration. One also can show readily from the above hydrolysis constants that the species Hg^{+2} and $HgOH^+$ are present at too small concentrations to be effective for the dissociation field effect. A charge neutralization process, the only kind giving rise to a measurable second Wien effect, involving these species is improbable anyway. An equilibrium constant for

$$HgOHCl \rightleftharpoons HgOH^+ + Cl^- \qquad (9)$$

has not been reported. An estimate of the maximum concentration of HgOHCl in aqueous $HgCl_2$ solution might be possible from the Raman spectrum.[14] The mixed ligand complex HgOHCl has a net dipole moment in contrast to $Hg(OH)_2$. Since water is a polar solvent, it also should stabilize HgOHCl somewhat.[15] One may expect dissociation constants of HgOHCl with respect to $HgOH^+$ or $HgCl^+$ which correspond to those for $HgCl_2$ and $Hg(OH)_2$ (with respect to $HgCl^+$ or $HgOH^+$, respectively). We therefore have made the assumption that eq. 6 is closely approximated by

$$[H^+] \approx [HgOHCl] + [Hg(OH)_2] \qquad (10)$$

Equilibrium 9 probably makes no significant, direct contribution to the observed second Wien effect because of a combination of two factors, neither one of which alone would preclude such a contribution: the concentration of HgOHCl is low ($\leq [H^+]$) and the dissociation constant for (9) is probably smaller than that for equilibrium 1. Thus equilibrium 1 is mainly responsible for the observed relaxation, although some small contribution of equilibrium 9 which is coupled to (1) might be present (*cf.* below). It should be mentioned that the hydrolysis of mercury compounds meanwhile has been shown also by means of other relaxation techniques. The data will be reported elsewhere.

In Table II we give values of k_R in equilibrium 1 where we have used the approximations

$$\begin{gathered} [HgCl^+][Cl^-]/[HgCl_2] = K_1 \\ C_0 \approx [HgCl_2] \\ [H^+] \approx [HgOHCl] + 2[Hg(OH)_2] \\ [Cl^-] \approx [HgCl^+] + [HgOHCl] \\ \tau = [k_R(K_1 + [HgCl^+] + [Cl^-])]^{-1} \end{gathered} \qquad (11)$$

The values of the specific rate k_R were obtained with

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(6) S. S. Joshi and D. N. Solanki, *J. Indian Chem. Soc.*, **14**, 323 (1937); **17**, 627 (1940).

(7) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **6**, 747 (1952).

(8) L. G. Sillén, *ibid.*, **3**, 539 (1949).

(9) Conservation of H and OH ($H^+ \gg 10^{-7}$ M).

(10) Conservation of Hg.

(11) Conservation of Cl.

(12) G. Anderegg, G. Schwarzenbach, M. Padmoyo, and O. F. Borg, *Helv. Chim. Acta*, **41**, 988 (1958).

(13) K. Damm and A. Weiss, *Z. Naturforsch.*, **10b**, 534 (1955).

(14) G. Allen and E. Warhurst, *Trans. Faraday Soc.*, **54**, 1786 (1958).

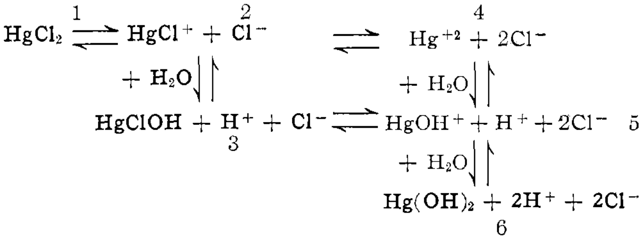
(15) T. G. Spiro and D. N. Hume, *J. Am. Chem. Soc.*, **83**, 4305 (1961).

TABLE II

VALUES OF THE SPECIFIC RATE k_R FOR $HgCl^+ + Cl^- \rightarrow HgCl_2$ CALCULATED FROM THE DATA IN TABLE I AND EQ. 11

c_0, mole/l.	k_R, M^{-1} sec.$^{-1}$ ($K_1 = 3.3 \times 10^{-7}$)
9.8×10^{-3}	7.7×10^{9}
7.9×10^{-3}	7.6×10^{9}
3.9×10^{-3}	4.4×10^{9}

$K_1 = 3.3 \times 10^{-7}$ M, a value that follows directly from eq. 4 and 5. This value was not corrected for zero ionic strength. However, it may be more realistic than the corrected "thermodynamic" equilibrium constant,[8] which should be somewhat low due to neglect of HgOHCl in the determination of K (literature value). The values of k_R in Table II agree well with rate constants for similar reactions of Hg^{+2} compounds as well as with those for reactions of Pb^{+2} and Ba^{+2}, which were determined by means of other relaxation methods.[16] The most reliable values seem to be around 7×10^9 M^{-1} sec.$^{-1}$. The rate constants obtained from the above evaluation still may include some systematic errors as a consequence of the very approximative evaluation. The true reaction mechanism is not so simple that it can be represented by eq. 1. There is a coupling of reaction 1 with the hydrolysis steps, which may be represented by the scheme



$$\begin{tikzcd}
\overset{1}{\mathbf{HgCl_2}} \arrow[r, shift left] & \mathbf{HgCl^+} \arrow[l, shift left] + \overset{2}{\mathbf{Cl^-}} \arrow[r, shift left] \arrow[d, shift right, "+ \mathbf{H_2O}"'] & \overset{4}{Hg^{+2} + 2Cl^-} \arrow[l, shift left] \arrow[d, shift right, "+ H_2O"'] \\
& \mathbf{HgClOH} + \underset{3}{\mathbf{H^+}} + \mathbf{Cl^-} \arrow[u, shift right] \arrow[r, shift left] & HgOH^+ + H^+ + 2Cl^- \quad 5 \arrow[l, shift left] \arrow[u, shift right] \arrow[d, shift right, "+ H_2O"'] \\
& & \mathbf{Hg(OH)_2} + \underset{6}{\mathbf{2H^+}} + \mathbf{2Cl^-} \arrow[u, shift right]
\end{tikzcd}$$

Only the species indicated by bold types are present in appreciable concentrations. We may consider two limiting cases

(1) The major part of hydrolysis products is present in the form of $Hg(OH)_2$ rather than HgOHCl ($HgOH^+$ and Hg^{+2} are negligible anyway). Then the only step we have to consider is the equilibrium 1–2, as was done in the above evaluation. (The hydrolysis steps do not show an appreciable effect, since the stages 3, 4, and 5 are only present at negligible concentrations and there is no other coupling from 2 to 6.) The results for this single step equilibrium 1–2 are given in Table II.

(2) For the other limiting case we assume that the major part of hydrolysis products is present in the form of HgOHCl. Then we have $[H^+] = [HgOHCl]$. We get a coupling between 1–2 and 2–3, represented by a spectrum of two relaxation times which are related to the normal modes of the coupled system. From the rate equations and conservation conditions we obtain these relaxation times[17] as roots of the characteristic equation

$$\frac{1}{\tau_{1,2}} = -\frac{\alpha_{11} + \alpha_{22}}{2}\left[1 \pm \sqrt{1 - \frac{4(\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21})}{(\alpha_{11} + \alpha_{22})^2}}\right] \quad (12)$$

with

$$\alpha_{11} = -\{k_{12} + k_{21}([HgCl^+] + [Cl^-])\}$$
$$\alpha_{22} = -\{k_{23} + k_{32}([HgClOH] + [H^+])\}$$
$$\alpha_{12} = -k_{21}[Cl^-]; \quad \alpha_{21} = -k_{23}$$

Only a relatively small fraction of the total field effect will be related to τ_1, which is governed by the hydrolytic rate constant k_{23} (as the largest quantity in $\alpha_{11} + \alpha_{22}$). The observed dispersion of the relatively large fraction of the field effect ($\tau \approx 10^{-6}$ sec.) is more likely to be associated with τ_2, which can be expressed simply as $-[\alpha_{11} - \alpha_{12}]$, since $\alpha_{22} \approx \alpha_{21}$ (both given by k_{23}) and $\alpha_{22}, \alpha_{21} \gg \alpha_{12}, \alpha_{11}$.

The quantity $-(\alpha_{11} - \alpha_{12}) = k_{12} + k_{21}[HgCl^+]$ is very similar to the relaxation time of the one-step system (eq. 1), as calculated above. In this case, however, we should expect two dispersion steps (of which the second at shorter times is relatively small). This seems to be indicated by the experimental value for $\omega\tau \approx 10$ in Fig. 1. As a consequence the relaxation time would be somewhat longer since the relative decrease of the amplitude in the first step occurs then at lower frequencies. This effect, however, compensates almost completely with shortening of the relaxation time $\tau = (k_{12} + k_{21}[HgCl^+])^{-1}$ as compared with eq. 2, $\tau = [k_{12} + k_{21}([HgCl^+] + [Cl^-])]^{-1}$, so that from both limiting cases almost the same rate constants result. Therefore a figure of 5×10^9 to 1×10^{10} M^{-1} sec.$^{-1}$ should be quite reliable for the rate constant of reaction 1. As mentioned above this figure agrees with values found for Pb^{+2} and Ba^{+2}. It is higher than for smaller divalent cations like Mn^{+2}, Co^{+2}, Mg^{+2}, but is about an order of magnitude lower than those found for protolytic or hydrolytic reactions (*i.e.*, reactions involving H^+ or OH^-) also determined from the dispersion of the dissociation field effect[5,18,19] found in those systems.

Acknowledgment.—E. M. E. is grateful to the National Science Foundation for a postdoctoral fellowship held in the course of this work.

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[16] M. Eigen, G. Maass, and W. Kruse, unpublished data.

[17] *Cf.* M. Eigen and L. De Maeyer, in A. Weissberger, "Techniques of Organic Chemistry," 2nd Ed., Vol. VIII, Interscience Publ., New York, N. Y.

[18] M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, **82**, 5952 (1960).

[19] M. Eigen and E. M. Eyring, *ibid.*, **84**, 3254 (1962).

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The Molecular Weight and Stability of Cyclotriborazane, $B_3H_6N_3H_6$, in Liquid Ammonia[1]

BY S. G. SHORE AND C. W. HICKAM

Received August 23, 1962

Dahl and Schaeffer[2] have reported the preparation of the analog of cyclohexane in the boron–nitrogen system, $B_3H_6N_3H_6$. This is the first compound of empirical

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[1] Presented before the Inorganic Division at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962.

[2] G. H. Dahl and R. Schaeffer, *J. Am. Chem. Soc.*, **83**, 3032 (1961).