CONTRIBUTION FROM IIT RESEARCH INSTITUTE,
CHICAGO, ILLINOIS

Acid–Base Reactions in Fused Mercuric Chloride

BY KLAUS F. GUENTHER

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Investigations by Bockris, Crook, Bloom, and Richards,[1] Janz and McIntyre,[2,3] and Janz and James[4] on the structure and properties of fused mercuric halides have shown that a high degree of covalency is retained in the molten state upon fusion of the mercuric halides. Jander and co-workers[5–8] applied the parent solvent concept to their investigations and showed that fused mercuric bromide and some other fused salts of predominantly covalent character exhibit the typical features of nonaqueous ionizing solvents.[9–10] One characteristic of nonaqueous ionizing solvents is that acid–base reactions can be performed in the system. The objective of the present investigation was to determine to what extent such reactions occur in fused mercuric chloride and to investigate some of these reactions in detail.

Experimental

The reactions between compounds of acid and basic character in fused $HgCl_2$ were investigated by conductometric titrations. The change in conductivity was measured as a function of the composition by a General Radio Corporation impedance bridge, Type 1650A, at 1000 c.p.s. The reactions were performed in a demountable Pyrex conductance cell which contained two blank platinum electrodes and provision for measuring temperature *in situ*. The cell constant was determined at 25° with 0.01 *N* aqueous KCl solution. The cell was placed in a $NaNO_2$–KNO_3 heating bath. Nearly the whole cell was submerged in the salt bath to prevent sublimation of the $HgCl_2$ to colder parts of the vessel. All experiments were performed at 281°.

The compounds used were reagent grade; 20 g. of $HgCl_2$ was used in each experiment, and the specific conductivity of the $HgCl_2$ was 3.8×10^{-5} mho cm.$^{-1}$ at 281°. The acid or the base was dissolved or suspended in the $HgCl_2$ melt, and increasing amounts of the corresponding compound were added. $Hg(ClO_4)_2$ solutions were prepared by mixing small amounts of $Hg(ClO_4)_2 \cdot 9H_2O$ with 20 g. of $HgCl_2$ and melting. An attempt to prepare a solution of $Hg(NO_3)_2$ in $HgCl_2$ by the same technique was unsuccessful.

The breaks in the conductometric titration curves indicated the formation of compounds. To verify their formation these compounds were prepared chemically by dissolving equivalent amounts of the corresponding substances in approximately 20 g. of $HgCl_2$. After the melt solidified, the contents were pulverized and extracted with ether in a Soxhlet apparatus until the weight was constant. The insoluble products which contained mercury and/or chloride were analyzed by gravimetric determination of these elements. In substances not containing mercury or chloride, the anion was determined. The formulas of the isolated compounds given in Table I were calculated from these analytical results.

TABLE I
ACID–BASE REACTIONS IN FUSED MERCURIC CHLORIDE[a]

Acid	Base	Acid–base mole ratio at which breaks in curves occurred	Isolated compounds	Solubility of isolated compounds in fused $HgCl_2$
$Hg(ClO_4)_2$[b]	NaCl	1:2	$NaClO_4$	Insoluble
	KBr	*1:2*	*$KClO_4$*	
$Hg(NO_3)_2$	NaCl	1:2	$NaNO_3$	Insoluble
$Hg(NO_3)_2$	KCl	1:2	KNO_3[c]	Soluble
	KBr	*1:2*	*KNO_3*	
$HgSO_4$[b]	NaCl	1:2	Na_2SO_4	Insoluble
	KBr	*1:2*	*K_2SO_4*	
		1:1	$Na_2SO_4 \cdot HgSO_4$	...
		1:1	*$K_2SO_4 \cdot HgSO_4$*	
$HgSO_4$	TlCl	1:2	Tl_2SO_4	Soluble
	TlBr	*1:2*	*Tl_2SO_4*	
		1:1	$3TlCl \cdot 3HgSO_4 \cdot 2HgCl_2$	Soluble
		1:1	...	
$HgSO_4$	$PbCl_2$	1:1	$PbSO_4$	Insoluble
	$PbBr_2$	*1:1*	*$PbSO_4$*	
$HgSO_4$	$C_{13}H_9N$	1:2	$2C_{13}H_9N \cdot 6HgCl_2 \cdot HgSO_4$	Soluble
		2:1	$C_{13}H_9N \cdot 3HgCl_2 \cdot 2HgSO_4$	...
		1:1, 3:2	...	...
$HgCrO_4$	NaCl	1:2	Na_2CrO_4	Soluble
		1:1	$Na_2CrO_4 \cdot HgCrO_4$[c]	Soluble
		3:2, 2:1		
$PbCl_2$	NaCl	1:2	$Na_2[PbCl_4]$	Soluble
		1:1	$Na[PbCl_3]$	Soluble

[a] Results of investigation in fused $HgBr_2$ by Jander and Brodersen[5] are given in italics. [b] Dissolved acid titrated with base; otherwise the bases were titrated with acid. [c] Approximate composition.

When reactions were performed with acridine, the tubes containing the reaction mixture were sealed under vacuum to avoid loss of the volatile compound. Because acridine–mercuric chloride compounds are slightly soluble in ether, the composition of these compounds was determined by plotting the weight loss during extraction as a function of extraction time and extrapolating the resulting curve to time zero.

Results

Table I lists the acid–base reactions performed, the mole ratios at which the conductometric titration curve showed a definite break, the compounds which were isolated from the melt, and the solubilities of these compounds in fused $HgCl_2$. For comparison, the corresponding reactions in fused $HgBr_2$ are also included in Table I (italics). A 0.064 *M* solution of $Hg(ClO_4)_2$ in fused $HgCl_2$ had an equivalent conductivity of 5.2 mhos cm.^{2} equiv.$^{-1}$, which was 36% lower after 5.5 hr. When freshly prepared solutions of $Hg(ClO_4)_2$ were titrated with NaCl, the equivalence point was found to be 3% below the calculated value. After 5.5 hr. the equivalence point was 63% below the calculated value. The conductivity of solutions of $Hg(ClO_4)_2$

(1) J. O'M. Bockris, E. H. Crook, H. Bloom, and N. E. Richards, *Proc. Roy. Soc.* (London), **A255**, 558 (1960).
(2) G. J. Janz and J. D. E. McIntyre, *Ann. N. Y. Acad. Sci.*, **79**, 790 (1960).
(3) G. J. Janz and J. D. E. McIntyre, *J. Electrochem. Soc.*, **109**, 842 (1962).
(4) G. J. Janz and D. W. James, *J. Chem. Phys.*, **38**, 902, 905 (1963).
(5) G. Jander and K. Brodersen, *Z. anorg. allgem. Chem.*, **261**, 261 (1950); **262**, 33 (1950); **264**, 57, 76, 91 (1951); **265**, 117 (1951).
(6) G. Jander and K. H. Swart, *ibid.*, **299**, 252 (1959); **301**, 54, 80 (1959).
(7) G. Jander and J. Weis, *Z. Elektrochem.*, **61**, 1275 (1957); **62**, 850 (1958); **63**, 1037 (1959).
(8) G. Jander and K. Guenther, *Z. anorg. allgem. Chem.*, **297**, 81 (1958); **298**, 241 (1959); **302**, 155 (1959).
(9) L. F. Audrieth and J. Kleinberg, "Nonaqueous Solvents," John Wiley and Sons, New York, N. Y., 1953.
(10) G. Jander, "Die Chemie in Wasseraehnlichen Loesungsmitteln," Springer, Berlin, 1949.

in fused $HgCl_2$ decreased linearly on addition of NaCl until the mole ratio $Hg(ClO_4)_2$:2NaCl was reached. Thereafter the conductivity of the solution increased rapidly.

Solutions of $Hg(NO_3)_2$ in fused $HgCl_2$ could not be prepared. When $Hg(NO_3)_2 \cdot H_2O$ was dissolved in the melt, rapid evolution of NO_2 occurred.

A 0.1 *M* solution of acridine showed an equivalent conductivity of 100 mhos cm.^{2} equiv.$^{-1}$. Solutions of acridine in $HgCl_2$ gave, after extraction of excess $HgCl_2$ with ether, green needles with the composition $1C_{13}H_9N \cdot 3HgCl_2$.

Discussion

Because of the close chemical and physical resemblance of mercuric bromide and mercuric chloride, a similarity of the acid–base reactions in both systems can be expected. Table I shows that in principle this is the case. $Hg(ClO_4)_2$, $Hg(NO_3)_2$, and $HgSO_4$ acted as acids in both solvent systems. Alkali and heavy metal bromides in fused $HgBr_2$ and alkali and heavy metal chlorides in fused $HgCl_2$ acted as bases, forming the corresponding salts in neutralization reactions. It is also evident from the table that some conductometric titration curves exhibited several breaks corresponding to different acid–base mole ratios. These breaks can be attributed to the formation of neutral salts and of acid salts which are thought to contain HgBr and HgCl groups. In addition to these similarities we found some differences between acid–base reactions in both solvent systems; moreover, we performed some other types of reactions which were not done in fused $HgBr_2$.

Although the titration curves obtained by using fused $HgBr_2$ as the solvent indicated the formation of acid salts, these salts could not be isolated from the melt. In all instances the acid salts decomposed and gave salts which did not contain bromine. In the case of $HgCl_2$, however, chlorine-containing salts could be isolated, for example, $3TlCl \cdot 3HgSO_4 \cdot 2HgCl_2$. Since the results in Table I show that $HgSO_4$ is a dibasic acid in fused $HgCl_2$ and since the base:acid mole ratio in $3TlCl \cdot 3HgSO_4 \cdot 2HgCl_2$ is 1:1, this compound can be considered an acid salt and thus be formulated as $3Tl(HgCl)SO_4 \cdot 2HgCl_2$. In a few instances, the acid salts in $HgCl_2$ were unstable and behaved like the acid salts in the $HgBr_2$ system. For example, in the case of $Na(HgCl)SO_4$, decomposition occurred yielding $Na_2SO_4 \cdot HgSO_4$ and $HgCl_2$.

The high equivalent conductivity of solutions of $Hg(ClO_4)_2$ and the shape of the conductometric titration curves obtained by titration with NaCl (see Results section) showed that $Hg(ClO_4)_2$ was the strongest of the acids investigated. $Hg(ClO_4)_2$ was likewise the strongest acid in fused $HgBr_2$. The decrease in conductivity of solutions of $Hg(ClO_4)_2$ in fused $HgCl_2$ and the change in the equivalence point on titration with NaCl with time (see Results section), however, indicate that solutions of $Hg(ClO_4)_2$ in fused $HgCl_2$ were not stable over long periods of time. Solutions of $Hg(ClO_4)_2$ in $HgBr_2$ were stable. Solutions of $Hg(NO_3)_2$ were likewise stable in fused $HgBr_2$ and unstable in fused $HgCl_2$. Since the experiments in fused $HgCl_2$ were performed at a 40° higher temperature than those in fused $HgBr_2$, it is reasonable to assume that decomposition of the $Hg(ClO_4)_2$ and $Hg(NO_3)_2$ in fused $HgCl_2$ resulted from the higher temperature.

Despite the instability of $Hg(NO_3)_2$ solutions in fused $HgCl_2$, it was possible to interact $Hg(NO_3)_2$ with alkali chlorides, but only when the alkali chlorides were titrated with the acid (Table I). Under these conditions, the $Hg(NO_3)_2 \cdot H_2O$ reacted immediately with the alkali chloride forming the corresponding salt while the crystal water evaporated.

Acridine behaved as a base in the $HgCl_2$ melt and its solutions showed a high conductivity. Moreover, its compounds isolated from the $HgCl_2$ melt contained solvent molecules (see Results section). Investigations of other nonaqueous systems such as fused $AsBr_3$[8] have shown that some aliphatic and aromatic amines behave similarly in these systems. This behavior probably results from the lone electron pair of the nitrogen in these substances causing an affinity to electropositive groups.

With NaCl, $PbCl_2$ acted as an acid in fused $HgCl_2$; with $HgSO_4$ it behaved as a base (Table I). This behavior illustrates the amphoteric character of $PbCl_2$ in fused $HgCl_2$.

CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Preparation and Resolution of a Five-Coordinate Complex: Bisacetylacetone-propylenediiminooxovanadium(IV)

BY K. RAMAIAH, F. E. ANDERSON, AND DEAN F. MARTIN

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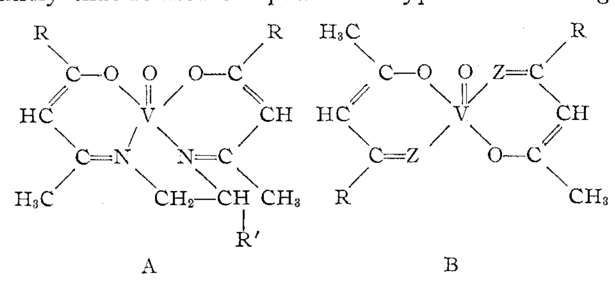
Recent structural analysis of bis(2,4-pentanediono)-oxovanadium(IV)[1] has established that this compound is an example of a five-coordinate complex and that the structure is nearly square pyramidal. It seemed likely that related compounds of type A and B might



A: $R = CH_3$, $R' = CH_3$

B: $R = CH_3$, $Z = NR'$; $R = C_6H_5$, $Z = O$

(1) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).