

complex, and (2) an allyl complex in which one of the chlorines or an additional hydrogen has added to the ring. The latter possibility merits serious consideration in view of the recent finding that butadiene-palladium chloride appears to be an allyl complex.<sup>4</sup> However, the chlorine attached to carbon in these allyl complexes has been found to be labile and readily displaced by alkoxy. No such alkoxy compound has been found in the case of the gold complexes. When an ethanolic solution of chloroauric acid is warmed with 1,5-cyclooctadiene in the presence of sodium carbonate, I is formed in place of II.

Compound I is therefore tentatively identified as an aurous and II as an auric complex of 1,5-cyclooctadiene. The formulation of I as an olefin complex is consistent with the identification of the infrared absorption at 1530 and 1520  $\text{cm}^{-1}$  as being due to a carbon double bond stretching frequency. Infrared absorptions in I and II at 3000  $\text{cm}^{-1}$  are identified as being due to olefinic CH stretching frequencies.

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GENERAL ELECTRIC CO. RESEARCH LABORATORY A. J. CHALK  
SCHENECTADY, NEW YORK

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### Effect of Inert Gas Pressure and Solubility on Electrical Conductance in Fused Salts

Sir:

We wish to present a preliminary report on recent data resulting from a study of the mechanism of electrical conductance in pure fused salts.

A 500-ml. capacity Inconel metal bomb, Type A24-3HC5 of the Parr Instrument Co., was fitted with two CONAX thermocouple glands packed with a natural magnesium silicate. One of these glands contains a Chromel-Alumel thermocouple, and the other contains a pair of 20-gauge platinum wires for conductance electrodes. Pyrex bomb liners were prepared with capillary conductance cells fixed rigidly within them. In a typical experiment, such a liner-cell is charged with about 450 g. of dry  $\text{NaNO}_3$  weighed to the nearest 0.5 g. Argon is admitted at room temperature into the sealed, evacuated bomb, containing the liner-cell and its salt charge, to a desired pressure. The number of moles of Ar introduced is calculated with the aid of the compressibility factor chart of Maslan and Littman<sup>1</sup> using the equilibrium values of pressure, room temperature, and the gas volume (known from the total volume of the bomb less the volumes of the liner-cell and its salt charge). The bomb is then heated in a furnace to a new temperature well above the melting point of  $\text{NaNO}_3$ . Conductance measurements are made on the fused salt at equilibrium temperature and pressure. The number of moles of gaseous Ar still remaining is calculated from the new values of equilibrium temperature, pressure, and gas volume (the old volume corrected for change in density of the salt and its compression) with the aid of the same compressibility chart. Decrease in moles of gaseous Ar is attributed to its solubility in the melt, the latter then being calculated. The gas is slowly evacuated from the system, and the latter is pumped out to remove all Ar from the melt. New conductance

readings are then taken on the gas-free melt at the same temperature.

First results for  $\text{NaNO}_3$ , using a capillary conductance cell of about 184- $\text{cm}^{-1}$  cell constant, indicate a 5.7% decrease in specific conductance when the melt at 369° was subjected to 362 atm. of Ar. The conductance measurements showed excellent precision for both the gas-saturated and gas-free melt, yielding specific conductances of 1.16  $\text{ohm}^{-1} \text{cm}^{-1}$  for the melt under pressure, and 1.23  $\text{ohm}^{-1} \text{cm}^{-1}$  for the normal liquid, both at 369°. Maximum experimental error in these values is believed to be less than  $\pm 0.01 \text{ohm}^{-1} \text{cm}^{-1}$ . The Henry's law constant determined for the solubility of Ar in fused  $\text{NaNO}_3$  under these conditions, based on two independent determinations, was  $18.7 \times 10^{-7}$  and  $19.6 \times 10^{-7}$  mole of Ar ( $\text{cm}^3$  of melt) $^{-1}$  atm. $^{-1}$ .

We believe that the observed conductance decrease under pressure is due to loss of free volume available for transport in the melt. In the hole theory of fused salts, the volume increase on melting,  $\Delta V$ , is attributed almost entirely to holes.<sup>2</sup> For  $\text{NaNO}_3$  this is 4.32  $\text{cm}^3$  mole $^{-1}$ , or a 10.7% volume increase.<sup>3</sup> The isothermal compressibility coefficient,  $\beta_T$ , for fused  $\text{NaNO}_3$  is about  $20.4 \times 10^{-12} \text{cm}^2 \text{dyne}^{-1}$  at 370°, based on interpolation of the data of Bockris and Richards.<sup>4</sup> Using these data in conjunction with a density of 1.87  $\text{g. cm}^{-3}$  for  $\text{NaNO}_3$  at 369°,<sup>5</sup> we arrive at an approximate upper limit loss of holes of about 8.8% due to compression by 362 atm. of Ar alone. Thus, if hole density is the major factor controlling conductance of a pure fused salt,<sup>6</sup> we would expect an approximate upper limit conductance decrease of fused  $\text{NaNO}_3$  of 8.8% under these conditions owing to compression alone. This is not irreconcilable with our observed 5.7% decrease. On the other hand, the theoretical molar density of holes in a pure fused salt is given as<sup>4</sup>

$$N_{\text{H}} = (\Delta V/0.68)(\gamma/kT)^{3/4}$$

where  $\gamma$  is the liquid-vapor surface tension,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature. Using this equation with a value of  $\gamma = 113.5 \text{ dynes cm}^{-1}$  at 369°,<sup>7</sup> in conjunction with the density of  $\text{NaNO}_3$ , the volume density of holes is  $4.86 \times 10^{21}$  holes  $\text{cm}^{-3}$ . Our average Henry's law constant together with this figure reveals that if Ar atoms dissolve by occupying existing holes, about 8.6% of the holes would be occupied and thereby removed from the conductance mechanism. This value is also not at odds with the observed conductance decrease. Considered separately, the theoretical conductance decrease due to either compression of the melt or gas solubility alone is in line with observation. There can be no doubt that free volume is reduced by compression of the melt, but it may be doubtful if inert gas molecules dissolve by occupying existing holes. The positive enthalpies of solution observed by Grimes, Smith, and Watson<sup>8</sup> may well indicate that solution occurs by the molecules

(2) H. Bloom, *Discussions Faraday Soc.*, **32**, 7 (1961).

(3) H. Schinke and F. Sauerwald, *Z. anorg. allgem. Chem.*, **304**, 25 (1960).

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(5) H. Bloom, *et al.*, *Transactions Faraday Soc.*, **49**, 1458 (1953).

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(7) C. C. Addison and J. H. Coldrey, *J. Chem. Soc.*, 468 (1961).

(8) W. R. Grimes, N. V. Smith, and G. M. Watson, *J. Phys. Chem.*, **62**, 862 (1958).

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creating their own holes, leaving most of the original holes intact. We therefore believe that loss of holes by compression may possibly be the major factor in the resulting diminution of conductance. Studies are being undertaken using other inert gases at the same pressure and temperature to ascertain if there is any dependence of conductance change on solubility.

DEPARTMENT OF CHEMISTRY  
KANSAS STATE UNIVERSITY  
MANHATTAN, KANSAS 66504

JAMES L. COPELAND  
WALTER C. ZYBKO

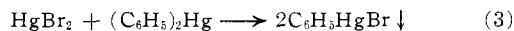
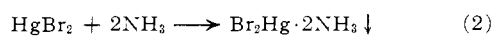
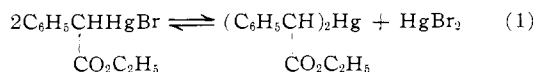
RECEIVED SEPTEMBER 18, 1964

### The Mechanism of Symmetrization of Ethyl $\alpha$ -Bromomercuri-phenylacetate by Diphenylmercury

Sir:

Conversion of organomercuric salts to diorganomercuric compounds, termed symmetrization, can be accomplished by a variety of reagents. These transformations occur by diverse mechanisms and represent important electrophilic reactions for mechanism studies.

The symmetrizations of esters of  $\alpha$ -halomercuriarylacetic acids have been extensively studied by Reutov and co-workers. Closely similar mechanisms were suggested for symmetrization by ammonia<sup>1</sup> (eq. 1 and 2) and by diphenylmercury (eq. 1 and 3).<sup>2</sup> Independ-



ent evidence was cited supporting each mechanism. The mechanistic proposals were considered mutually supporting since the first step in each is the same.

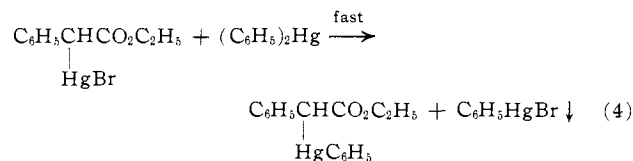
However, the kinetic evidence presented by Reutov and co-workers for the symmetrization by ammonia has been re-examined, and it has been shown that the proposed mechanism (eq. 1 and 2) would not give the observed kinetics.<sup>3</sup> The sole remaining evidence offered in support of Reutov's mechanism is the proposal that the reaction with diphenylmercury takes a similar course. A re-examination of this reaction, a summary of which is given here, has revealed that the mechanism proposed by Reutov and co-workers for symmetrization by diphenylmercury is also incorrect.

The reaction of ethyl  $\alpha$ -bromomercuri-phenylacetate (0.2 *M*) with diphenylmercury (0.1 *M*) was found to proceed in two stages. The first reaction, which is complete in less than 60 sec., yields as a precipitate 1 mole of phenylmercuric bromide for each mole of diphenylmercury. The second reaction requires about two weeks for complete reaction at room temperature and yields a second mole of phenylmercuric bromide.

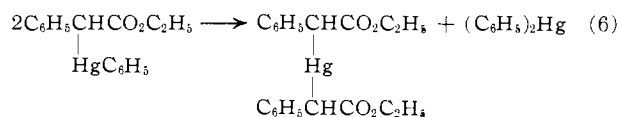
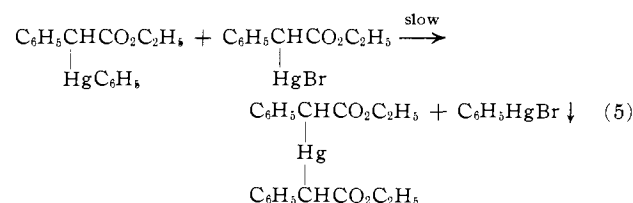
When alkylmercuric salt and diphenylmercury were allowed to react in chloroform solution in mole ratios of

4:1, 2:1, 1:1, and 1:2, the phenylmercuric bromide obtained in the fast reaction was found to correspond (95–99% yield) to the molar quantity of the reagent present in the lesser amount. Therefore, the stoichiometry of the fast reaction is 1:1. This finding negates the mechanism of Reutov and co-workers which requires a stoichiometry of 2:1.

The observed stoichiometry is consistent with formation of unsymmetrical diorganomercurial in the fast reaction (eq. 4). This material is slowly converted to symmetrical dialkyl and additional phenylmercuric



bromide either by eq. 5, or by eq. 6 and another re-



action equivalent to eq. 4.

Additional evidence which strongly supports this scheme was obtained by examination of the n.m.r. spectra of the reaction mixtures. The spectrum of the product obtained in the fast reaction (reagents in 1:1 molar quantities) is different from that of the symmetrical dialkylmercury compound, but is consistent in every respect with the spectrum expected of the unsymmetrical mercurial (eq. 4). The n.m.r. spectrum of the solution slowly changes with time and additional signals appear which correspond to diphenylmercury and the symmetrical dialkylmercurial. The signals of the original spectrum do not entirely disappear, but evidently decrease only until equilibrium is attained. When ethyl  $\alpha$ -bromomercuri-phenylacetate and diphenylmercury are reacted in 2:1 molar concentrations, the n.m.r. spectrum of the solution (phenylmercuric bromide precipitates) corresponds to a composite of the spectrum attributed above to the unsymmetrical alkylmercurial and unreacted ethyl  $\alpha$ -bromomercuri-phenylacetate. In time, these signals gradually disappear and a new set appears which corresponds to the spectrum of the symmetrical dialkylmercurial.

While the above results indicate the probable sequence of reactions for symmetrization, they do not provide evidence regarding the actual details of bond making and bond breaking.

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DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CALIFORNIA  
BERKELEY 4, CALIFORNIA

FREDERICK R. JENSEN<sup>4</sup>  
JOHN MILLER

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