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Dissociation of Ethoxy Methyl Carbenium Hexachloroantimonate in Methylene Chloride Solution. II. The Nature and Extent of the Dissociation

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ABSTRACT

Ethoxy methyl carbenium hexachloroantimonate has been synthesized as a model compound for the propagating species in the cationic polymerization of the vinyl ethers. Its degree of dissociation in methylene chloride has been studied as a function of concentration by using the method described in Part I. A simple one $\rightleftharpoons$ two dissociation was found. The degree of dissociation, however, was less than that found with a typical initiator such as triphenyl methyl hexachloroantimonate.

INTRODUCTION

In the previous paper [1] some observations were made regarding the measurement of the electrical conductivity of very low conductivity organic solutions and a suitable method was presented. In this paper the synthesis of ethoxyl methyl carbenium hexachloroantimonate, a model compound for the polymerization of the vinyl ethers, and the nature and degree of its dissociation in methylene chloride are described.

THEORETICAL

For most organic reactions in solution involving ions, the equilibrium (1) between various states of active species should be considered:

$$\begin{array}{llll} RX \rightleftharpoons & R^+X^- \rightleftharpoons & R^+//X^- \rightleftharpoons & R^+ + X^- \\ \text{molecular} & \text{contact} & \text{solvent} & \text{free} \\ \text{species} & \text{ion pair} & \text{separated} & \text{ions} \\ & & \text{ion pair} & \end{array} \qquad (1)$$

It is clear from conductivity studies of various catalyst system in methylene chloride, that the stable carbenium ion salts are almost completely dissociated at the concentrations used for many polymerization studies [2-4]. Ledwith [5] has presented cogent arguments that the growing chain ends should be even more dissociated. However, this question has remained largely unresolved. To attempt to answer this question, a model system, $CH_3-CH_2-O-\overset{+}{C}HCH_3-SbCl_6^-$, ethoxy methyl carbenium hexachloroantimonate, was synthesized, and its degree of dissociation in methylene chloride was determined by electrical conductivity measurements.

Theoretically, for a one $\rightleftharpoons$ two dissociation, say

$$A \rightleftharpoons R^+ + Q^-, \ K \qquad (2)$$

if the initial concentration of the reagent is C_0, and if $[R^+] = [Q^-] = i$ (all concentrations in mole/liter), and the degree of ionization is defined as $\alpha \equiv 1/C_0$, then

$$K = i^2/(C_0 - i) = C_0\alpha^2/(1 - \alpha) \tag{3}$$

$$C_0\alpha^2 + K\alpha - K = 0 \tag{4}$$

Equation (4) has the solutions:

$$\alpha = -K \pm \sqrt{K^2 + 4KC_0}/2C_0 \tag{5}$$

If the specific conductance of the system is κ(ohm^{-1} cm^{-1}), and the ionic conductance of the system is defined as:

$$\Lambda_T \equiv 10^3\ \kappa/i$$

then

$$\Lambda_T = 10^3\ \kappa/C_0 \tag{6}$$

so,

$$\alpha = 10^3\ \kappa/C_0\Lambda_T \tag{7}$$

Substituting Eq. (7) into Eq. (5) yields

$$\kappa = (-K \pm \sqrt{K^2 + 4KC_0}/2 \times 10^3)\ \Lambda_T \tag{8}$$

Because κ is always positive, hence

$$\kappa = (K\Lambda_T/2 \times 10^3)\left[\sqrt{1 + (4C_0/K)} - 1\right] \tag{9}$$

There are two special cases which can be used to simplify Eq. (9). Case 1. If $4C_0/K \ll 1$,

$$[1 + (4C_0/K)]^{1/2} \approx 1 + (2C_0/K) \tag{10}$$

so,

$$\kappa \approx \Lambda_T C_0/10^3 \quad (11)$$

This means that κ increases linearly with C_0.

Case 2.
If $4\,C_0/K \gg 1$

$$\kappa \approx (k\Lambda_T/2 \times 10^3)\,[2\sqrt{C_0/K} - 1] \quad (12)$$

$$\kappa \approx (K^{1/2}\Lambda_T C_0^{1/2}/10^3) - (K\Lambda_T/2 \times 10^3) \quad (13)$$

This means that κ increases linearly with $C_0^{1/2}$, the slope is equal to $K^{1/2}\Lambda_T/10^3$, and the intercept is $-K\Lambda_T/2 \times 10^3$.

But, for a two ⇌ two dissociation [5],

$$A + B \rightleftharpoons R^+ + Q^-,\ K \quad (14)$$

and

$$\kappa = 10^{3}\ \Lambda_T K^{1/2} C_0/(1 + K^{1/2}) \quad (15)$$

So, κ increases linearly with C_0 and through the origin.

EXPERIMENTAL

Materials

α-Chloroethyl ethyl ether (αCEE) was synthesized by a method described previously [6].

The solvent, CH_2Cl_2, was purified by the method described previously [7-9]. $SbCl_5$ used for this study was a pure commercial product.

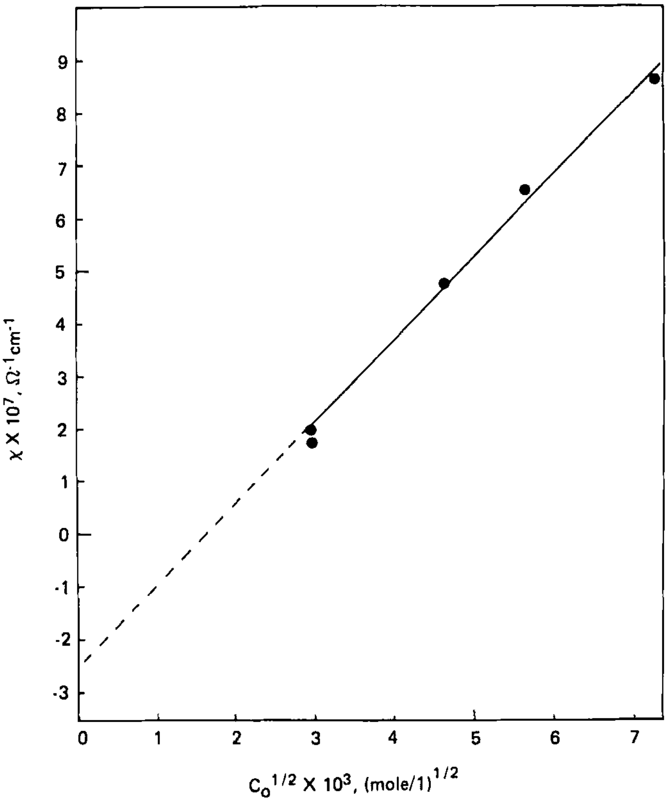

FIG. 1. Relationship between concentration and specific conductivity of ethoxy carbenium hexachlorantimonate in methylene chloride solution at -6°C.

Instruments

The conductivity cell, oscillator (frequency generator) and vacuum tube voltmeter (VTVM) were described in detail Part I of this series [1].

Procedures

The preparations of the vials of $SbCl_5$ and αCEE have been described previously [2]. For the conductivity studies, the lower half of the

TABLE 1. Effect of Concentration in Methylene Chloride on the Degree of Dissociation α of Trityl and Ethoxy Methyl Carbenium Ion Hexachloroantimonates

	α	
C_0 ($\underline{M}$)	$[Ph_3C^+]^a$	$[\alpha CEE^+]^b$
1.0×10^{-5}	(0.97)	0.62
1.9×10^{-5}	(0.95)	0.51
2.1×10^{-5}	(0.94)	0.49
3.1×10^{-5}	(0.90)	0.43
4.8×10^{-5}	(0.88)	0.37
$< 10^{-3}$	> 0.42	> 0.10

[a] $K_d = 3.1 \times 10^{-4}$ $\underline{M}$ at 0°C, [4].

[b] $K_d = 1.0 \times 10^{-5}$ $\underline{M}$ at -6°C (this study).

[c] Parenthetical values were calculated by assuming that the equilibrium is the one $\rightleftharpoons$ two type.

adiabatic calorimeter was replaced by a conductivity cell, designed to fit the upper half (equipped with stirrer, thermocouple, vial-holder and breaker, and a side arm for distillation).

The vials which contained αCEE and $SbCl_5$ were put in the holder. The flask containing the purified CH_2Cl_2 was sealed to the side arm, the solvent being still protected by a breakseal.

The conductivity cell was evacuated at 10^{-3} Torr for several hours, the temperature being kept under 0° C all the time to prevent any decomposition of the αCEE. Before the conductivity measurement, the circuits between the VTVM and generator were shorted, (see the schematic of experimental apparatus of part I [1]). The voltage of the VTVM was calibrated precisely. Then, the VTVM and generator were connected to the conductivity cell.

The vacuum pump was isolated and the breakseal crushed, the solvent was distilled from the storage flask (at room temperature) to the conductivity cell (-6° C). After this distillation, it was checked that the conductivity of CH_2Cl_2 was still as low as 10^{-9} ohm^{-1} cm^{-1} (the frequency was set at 100 Hz), to make sure that no impurity has been introduced during the various operations.

The two vials were then crushed with the breaking rod, and the conductivity itself was determined. The frequency was adjusted to 1000 Hz, the optimum frequency of the operation.

RESULTS AND DISCUSSION

In this study, the initial concentration of the reagent C_0 was varied over the range of $1.0 \times 10^{-5} \sim 5.0 \times 10^{-4}$ M at -6°C. Figure 1 shows unequivocally that a one $\rightleftharpoons$ two dissociation was involved. The final result was calculated by using the slope and intercept of the plot. The equilibrium constant was 1.0×10^{-5} mole/liter. This is less than found for the trityl hexachloroantimonate itself and leads to degrees of dissociation of only 20-50% at the concentrations used for most reported kinetics studies [10]. Assuming that the free ions are propagating much faster than ion pairs, this implies that the reported propagation rate constants can be low by factors of 2-5. The difference in the fraction dissociated (α) for both the initiator and the model compound are given in Table 1 for various concentrations.

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