

Exchange of Chlorine between Acetyl Chloride and Benzyldimethylphenylammonium Chloride

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Complete exchange of chlorine has been observed between benzyldimethylphenylammonium chloride containing radioactive chlorine-36 and acetyl chloride within 5 minutes. The results favour self-ionisation of the acetyl chloride.

The self-ionisation of acetyl chloride¹ has been recently proposed to explain the reactions occurring² in this solvent. Acetyl chloride is supposed to ionise as:



If the ionisation takes place as represented above, the addition of radioactive chloride ion will rapidly introduce radioactive chlorine in acetyl chloride. Benzyldimethylphenylammonium chloride ($\text{C}_7\text{H}_7\text{NPhMe}_2$)Cl, which is fairly soluble in acetyl chloride, has been used in the exchange experiment because conductivity measurements¹ have shown that this substance dissolves in acetyl chloride to produce chloride ions. Exchange experiments have also been conducted with labelled sodium chloride, which is insoluble in acetyl chloride.

EXPERIMENTAL

All the chemicals and reagents used were of A. R. quality and their purities were tested before use. These were subjected to further purification, whenever necessary.

Tracer.—Chlorine-36 was obtained from the Radiochemical Centre, Antershan, England, in the form of 2*N*-HCl of specific activity of 116 micro curies per g. of chloride.

Preparation of Labelled Compounds.—3% Aqueous solution of benzyldimethylphenylammonium chloride, prepared by the method of Michler and Grandmann³, was passed through an ion-exchange column of Amberlite IRA-410 in the OH form at the rate of 0.5 ml/min. The effluent containing benzyldimethylphenylammonium hydroxide was then exactly neutralised with HCl containing radioactive chlorine-36. The mixture was then subjected to vacuum distillation to remove water at 40-45°. The solid ($\text{C}_7\text{H}_7\text{NPhMe}_2$)Cl³⁶ was recrystallised from ethanol and ethyl acetate³. Finally it was dried over P_2O_5 *in vacuo*.

1. Paul and Sandhu, *Proc. Chem. Soc.*, 1957, 262.
2. *Ber.*, 1877, 10, 2079.
3. Ryan, *Canad. J. Chem.*, 1956, 34, 1683.

Sodium hydroxide solution was neutralised with HCl containing radioactive chlorine-36. The solution was evaporated to dryness and the solid NaCl* was dried over P_2O_5 in vacuo.

Preparation of Dry Acetyl Chloride.—Acetyl chloride dried over metallic sodium was distilled at room temperature (30-31°) under vacuum and collected in a bulb containing sodium metal, dried at 120° under vacuum.

Exchange Runs.—The exchange runs were carried out in a closed flow system with an arrangement to create vacuum and fitted with detachable bulbs with ground-glass joints, a manometer, and a guard tube of phosphorus pentoxide.

A known weight of the labelled compound, either benzyldimethylphenylammonium chloride or sodium chloride, was taken in the exchange vessel and was dried over P_2O_5 under vacuum at room temperature in the case of the former and at 110-20° in the case of the latter. Dry acetyl chloride was distilled under vacuum and condensed in the exchange vessel, cooled with dry ice. After 5 minutes of contact, a portion of acetyl chloride was distilled at room temperature under reduced pressure and condensed in a collector, cooled with dry ice. Similarly at various intervals of time, acetyl chloride was distilled and collected. The distillate was hydrolysed with cold distilled water and then acidified with HNO_3 (dil.). Chloride ion was precipitated as AgCl, centrifuged, washed with water and ethanol, and dried at 110-20°. Samples of silver chloride with thickness (at least 264 mg./cm²) greater than infinite thickness were mounted on an aluminium planchet and counted on thick aluminium sample holder with an end window (2.5 mg./cm² of aluminium) GM counter. All samples were counted under identical conditions. The correction for background radiation was made. In a few experiments thin samples were prepared for determining the specific activity of the samples. With such samples, corrections for self-absorption and self-scattering were applied. After removing acetyl chloride completely, the activity of the solid was measured in the form of silver chloride.

Stability of benzyldimethylphenylammonium chloride in boiling acetyl chloride was tested by estimating the chlorine content of the residue after the exchange runs. (Found: Cl, 13.98. Calc. Cl, 14.34%).

TABLE I

Exchange of chlorine between acetyl chloride and benzyldimethylphenylammonium chloride-36.

Active $(C_7H_7NPhMe_2)Cl^*$ taken = 0.5523 g. Acetyl chloride taken = 3.630 g.
Background counts/min. = 17. Sp. activity of the compound taken = 2.5×10^5 c/m/g. of Cl.

Time of contact.	Activity (counts/min.).	Remarks.
7 min.	111	Activity of acetyl chloride
12	109	Do
29	108	Do
..	110	Activity of the residual compound

TABLE II

Exchange of chlorine between acetyl chloride and sodium chloride-36.

Active sodium chloride* taken = 0.1558 g. Acetyl chloride taken = 4.3543 g.
 Sp. activity of sodium chloride-36 (before experiment) = 3.0×10^6 c/m/g. of Cl and
 (after experiment) = 3.2×10^6 c/m/g. of Cl. Background counts/min. = 15.

Time of contact.	Activity of acetyl chloride in the form of silver chloride (counts/minute).	Time of contact.	Activity of acetyl chloride in the form of silver chloride (counts/minute).
32 min.	0	25 hr.	3
93	3	48	0
210	0		

DISCUSSION

The results in Table I indicate that the activity of evolved acetyl chloride after different contact time is very nearly the same and is almost equal to that of benzyldimethylphenylammonium chloride. This suggests that the exchange of chlorine between the two component chlorides is complete within the time of separation. Exchange, involving reaction with water, is not possible because great care has been taken to remove moisture from the system. The possibility of induced exchange due to separation is completely excluded by the procedure followed in this investigation. Complete exchange observed in the dark eliminates the exchange by photochemical reaction.

As stated earlier, benzyldimethylphenylammonium chloride is known to produce chloride ions in acetyl chloride. Exchange of chloride ion by transfer of CH_3CO^+ , as indicated :



is not very plausible because both chloride ion and acetyl chloride are electron donors. The self-ionisation of acetyl chloride:



as proposed by Paul and others¹, can account for complete exchange of chlorine between acetyl chloride and benzyldimethylphenylammonium chloride. No exchange of chlorine has been observed between insoluble sodium chloride and acetyl chloride (Table II).