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Potentiometric Determination of Chlorides Formed by Radiolysis of Chlorobenzene in *n*-Hexane

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The method of potentiometric titration was used to determine the yield of chlorides radiolytically produced in solution of chlorobenzene in *n*-hexane. The results obtained suggest that this method is convenient for the determination of chlorides present in non-aqueous solution and could be applied particularly in chemical dosimetry.

Hydrochloric acid is one of the radiolytical products in irradiated organic solutions containing a chlorinated hydrocarbon. Those systems are of interest in radiation chemistry since at a sufficiently high concentration of chlorinated compounds the yield of hydrochloric acid may correspond to the yield of electrons formed in the system through the absorption of high energy radiation. Also, chlorinated hydrocarbons are an essential component of dosimetric systems proposed[1-3].

The concentration of radiolytically produced hydrochloric acid could be determined by measurements of either H^+ or Cl^- ions and the methods used so far include spectrophotometry[4], colorimetry[5], potentiometric pH measurements[6], oscillometry[7], and alkalimetric or mercurimetric titrations[3].

The sensitivity and accuracy of the analytical method are particularly important in establishing the usefulness of the system for dosimetric application. The well known potentiometric chloride titrations seem to be the most accurate, sensitive and easiest to perform even in cases of non-aqueous dosimetric systems. The purpose of the present communication is to illustrate the determination of radiolytically produced Cl^- ions by potentiometric titration carried out with an Ag/Ag_2S indicator electrode. The irradiated model system used was the solution of chlorobenzene in *n*-hexane.

EXPERIMENTAL

Materials

All chemicals were of analytical grade purity with exception of chlorobenzene (Riedel de Haen, tech.) which was distilled twice on a 170 cm column packed with glass spirals and the fraction boiling at 131.6 °C was collected.

The solution of $AgNO_3$ in ethanol used in all titrations was standardized at approximately 1×10^{-3} M by use of a standard NaCl solution.

Preparation and irradiation of samples

The solution of 1.956×10^{-3} M C_6H_5Cl in *n*-hexane was prepared volumetrically. 2 ml-samples were dried with P_2O_5 and degassed by a few cycles of freezing, evacuation and thawing, before being sealed off in Pyrex ampoules.

Irradiations were performed on a ^{60}Co source. The dose rate was determined by ferrous sulphate dosimetry and from these determinations the dose rate in *n*-hexane solution was calculated by applying corrections for electron density. After irradiation the samples were kept in liquid air until the time of analysis.

Emf. measurements

Emf. measurements were carried out by means of the cell[8]

Ag/AgBr | 0.01 M KBr | 0.001 M KNO_3 | test solution | Ag/Ag_2S

and a potentiometer (Derritron Instruments Ltd.) coupled with a galvanometer (Multiflex, Lange) of maximal sensitivity 6×10^{-10} A/mm and resistance of 7000 Ω. It is possible to use instead any of the commercial types of Ag/Ag_2S electrode or any reference electrode, *e. g.* a calomel electrode provided with a double junction in order to prevent the contamination of the sample solution with chloride ions.

Analysis for HCl

2 ml of aqueous solution of 0.3 M H_2SO_4 were added after the ampoule containing the frozen sample was opened. When the sample solution reached room temperature the two layers were vigorously agitated by shaking in order to ensure complete extraction of HCl from the organic layer. Then 1 ml of aqueous acidic solution was transferred to a beaker containing 10 ml of ethanol and then titrated with standardized 1×10^{-3} M $AgNO_3$ by means of a microdosimeter which made it possible to add 0.001 ml of the reagent with a fair degree of accuracy. During the titration the solution was stirred by a magnetic stirrer.

RESULTS AND DISCUSSION

The production of hydrochloric acid as a function of radiation dose is shown in Fig. 1 for 1.965×10^{-3} M chlorobenzene in *n*-hexane. Each point represents the mean of 2—4 independent measurements. The deviation from the mean was ± 1.5 per cent or less for chloride concentration above 1×10^{-4} M. The lowest concentration determined in the irradiated sample was approximately 5×10^{-5} M of chloride. The equivalence point in each single titration was established by Gran's method[9].

Obviously, the high precision and sensitivity of potentiometric titration made it possible to measure even small changes in HCl radiation yield. Consequently two straight lines should be plotted through the experimental points for the doses up to 7×10^{19} eV/g. Two radiation yields G_1 (HCl) and G_2 (HCl) which were estimated from two slopes amounted to 1.00 and 0.82, respectively. This probably reflects the influence of some secondary products on the process of HCl formation already in this initial period of radiolysis. However, at higher total doses ($> 7 \times 10^{19}$ eV/g) a continuous decrease in HCl yield normally occurs because of the substantial decrease in C_6H_5Cl concentration. Preliminary determinations of G (Cl^-) as a function of initial C_6H_5Cl concentration have shown that in the range from 0.982 M to $0.982 \times \times 10^{-3}$ M of chlorobenzene this value changes from 3.41 to 0.61.

Experience gained in this work suggests the suitability of potentiometric determination of chlorides in non-aqueous irradiated systems, particularly for the purpose of chemical dosimetry.
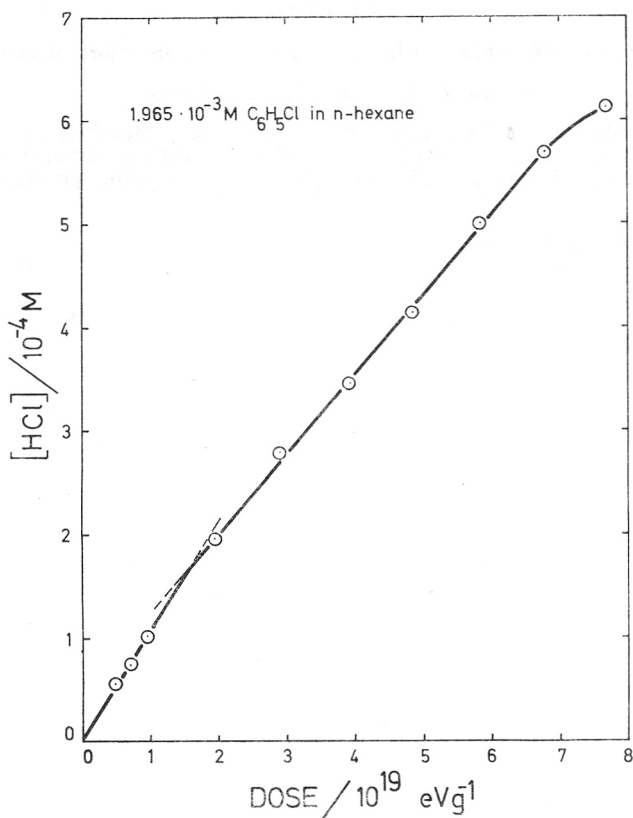
Fig. 1. **Production of HCl as** function of radiation dose during the radiolysis of 1.965×10^{-3} M C_6H_5Cl solution in n-hexane.

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SAŽETAK

Potenciometrijsko određivanje klorida nastalih radiolizom klorbenzena u n-heksanu

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Metodom potenciometrijske titracije određivan je prinos klorida nastalih radiolizom otopine klorbenzena u n-heksanu. Dobiveni rezultati ukazuju na prikladnost opisane metode za određivanje klorida u bezvodnom mediju, posebno u kemijskoj dozimetriji.

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