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Coördination of Silver Ion with Unsaturated Compounds. V. Ethylene and Propene

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The coördination of aqueous silver ion with ethylene and propene has been studied by a distribution method. The constants for the formation of a 1:1 complex are approximately the same for these two olefins. No significant amount of diolefin complex is formed by either hydrocarbon in the concentration range investigated but there is evidence for disilver complexes at high concentrations of silver ion.

The coördination complexes formed by silver ion with ethylene and propene are described in this report which thereby completes studies¹⁻⁴ of the argentation of the simpler olefins. The technique used in the study of these complexes and the symbolism used in their description are essentially the same as those employed in our earlier work.⁴

Experimental

Materials.—All of the inorganic chemicals and solutions were the same as those used earlier. Carbon tetrachloride was purified by passing into it a large excess of chlorine, irradiating the mixture with sunlight for 48 hours, and removing the chlorine by washing with dilute sodium hydroxide. After several washings with water the product was dried over calcium chloride and distilled. A blank test on the purified material showed that it neither absorbed nor liberated bromine or iodine.

Propene bromide was prepared from 2-propanol by dehydration and subsequent bromination. The crude product was distilled and then fractionated twice, b.p. 139.3–139.8° (uncor.) at 746 mm., n_D^{20} 1.5173, n_D^{20} 1.5200. These values for the boiling point and refractive index agree satisfactorily with those reported by Kahlbaum,⁵ b.p. 141.0° at 760 mm. and n_D^{20} 1.5198 and by von Zawidzki,⁶ n_D^{25} 1.51745.

Ethylene bromide was prepared from ethanol by dehydration and subsequent bromination; the crude product was recrystallized from methanol in a Dry Ice-isopropyl ether-bath. It was then washed twice with 80% sulfuric acid and with water until the wash water was neutral, and was subsequently dried over potassium carbonate. The purified ethylene bromide distilled at 129.7–129.8° (uncor.) at 746 mm.; the refractive index of the distillate was n_D^{20} 1.5359. These figures agree well with those reported by Anschütz,⁷ b.p. 129.5° at 745 mm., and by von Zawidzki,⁶ n_D^{25} 1.53601. When the recrystallization and subsequent washings, drying, and distillation were repeated, the boiling point and refractive index were found to be unchanged.

Preparation of Propene and Ethylene.—Ethylene and propene were prepared in an identical fashion, by the reaction of strip zinc with the corresponding dibromide diluted with an equal volume of 95% ethanol. The reaction was carried out in a 500-ml. three-necked flask fitted with a Friedrich condenser, a thermometer, and a vertical safety tube extending well below the surface of the reaction mixture and leading to an open erlenmeyer flask about 75 cm. above the reaction flask. The safety tube served as a convenient pressure gage during the generation of the gas. From the outlet of the Friedrich condenser the gas passed to a 20-cm. one-piece spiral wash bottle containing a 1:1 mixture of ethanol and water and then to another similar wash bottle containing pure water. Finally the gas was absorbed in two Friedrich-type gas wash bottles each of which contained about 200 ml. of carbon tetrachloride.

After the dibromide and the ethanol had been placed in

the reaction flask the whole system was swept out with nitrogen. Then a small portion of zinc was added and the mixture was heated very gently for about 30 seconds in order to start the reaction. Once started it proceeded quite rapidly without further heating; a cooling bath was usually necessary in the early stages of the reaction in order to prevent the evolution of gas from becoming too vigorous. The remainder of the zinc was added as needed, and the reaction was allowed to continue at room temperature for several hours until the carbon tetrachloride appeared to be saturated with the olefin. The solutions of the olefins in carbon tetrachloride were stored under an atmosphere of nitrogen in order to prevent the formation of peroxides which might interfere seriously with the analytical procedures.¹

Distributions.—The distributions were carried out at $25.00 \pm 0.03^\circ$; introduction of the solutions, stirring, and sampling were all carried out in the manner described earlier.^{4,8}

The Analytical Procedure.—In the earlier work, satisfactory analyses for the higher olefins and other unsaturated substances were made by bromination with acidified standard bromate-bromide solutions; the excess of bromine was determined iodometrically. Since it has been reported that bromine adds less rapidly to ethylene than to the higher olefins in water⁹ as well as in dry carbon tetrachloride¹⁰ and methylene chloride,¹¹ the suitability of the bromination procedure for the determination of ethylene required study. Because, as shown below, the method was found to be satisfactory for the determination of ethylene it was assumed likewise to be suitable for the determination of propene and no explicit study of the rate of bromination of propene was made.

Suida and Wesely⁹ studied the rate of absorption of ethylene when mixtures of ethylene and air were shaken with 0.005 *N* bromine water. They showed that all of the ethylene was absorbed in less than six minutes from a mixture which contained initially 10% of the olefin and that all of the ethylene disappeared in less than four minutes from a mixture containing originally only 7% of this compound. In all of our experiments in which the bromination mixture was homogeneous, that is, in the analyses of aqueous solutions of ethylene and of ethylene and the readily-dissociated silver ion-ethylene complex, the excess concentration of bromine was 0.003 *N* or greater and the bromination time was about fifteen minutes. It would appear that there should be no difficulty in obtaining quantitative bromination of the ethylene under these homogeneous conditions.

Several studies have been made of the rate of bromination of ethylene in the dark in carbon tetrachloride^{10,12,13} and although none of the results can be applied directly to the present work several observations are pertinent. The addition of bromine to ethylene is reported to be relatively slow in pure dry carbon tetrachloride but it is markedly accelerated by the presence of moisture¹⁰ and hydrogen bromide.¹² Davis claims that the greater part of the reaction takes place in the aqueous phase; he also states that

(8) Since the values of the constants were not observed to vary appreciably with time of standing of the distribution mixture, it was not thought necessary to use an all-glass system. Earlier it had been found necessary to eliminate all rubber stoppers in order to obtain reproducible results in the work with 2-pentene,³ although it was not necessary with the butenes.⁴

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(11) C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 2354 (1931).

(12) D. M. Williams, *ibid.*, 2911 (1932).

(13) P. W. Robertson, N. T. Clare, K. J. McNaught and G. W. Paul, *ibid.*, 335 (1937).

(1) S. Winstein and H. J. Lucas, *This Journal*, **60**, 836 (1938).

(2) H. J. Lucas, R. W. Moore and D. Pressman, *ibid.*, **65**, 227 (1943).

(3) H. J. Lucas, F. W. Billmeyer and D. Pressman, *ibid.*, **65**, 230 (1943).

(4) F. R. Hepner, K. N. Trueblood and H. J. Lucas, *ibid.*, **74**, 1333 (1952).

(5) G. W. Kahlbaum, *Z. physik. Chem.*, **26**, 626, 646 (1898).

(6) J. von Zawidzki, *ibid.*, **35**, 147 (1900).

(7) R. Anschütz, *Ann.*, **221**, 137 (1883).

"in solutions of carbon tetrachloride saturated with water and containing equimolar amounts of bromine and ethylene the bromine color disappears in a few minutes although in the absence of water the color may persist for a long time."

The applicability of the previously used bromination procedure to the determination of ethylene in carbon tetrachloride was tested as follows. Aliquot portions of a freshly prepared solution of ethylene in carbon tetrachloride were added to an excess of acidified aqueous bromate-bromide solution in evacuated flasks wrapped in dark cloth. The time of bromination was varied from 6 to 46 minutes and in addition certain of the mixtures were shaken mechanically during all or part of the period of bromination while others were allowed to stand essentially undisturbed. At the end of the period of bromination an excess of 2 *N* aqueous potassium iodide was added, the mixture was shaken for a few minutes *in vacuo* and the iodine which had been liberated was titrated at once with thiosulfate. These experiments showed conclusively that mechanical shaking was a practical necessity and that, with shaking, essentially complete bromination took place in less than 15 minutes. In the actual analyses of distribution mixtures, the bromination mixture was shaken for 15 to 20 minutes in the dark. The remainder of the analytical method was essentially that used earlier.⁴

Results

Distribution Ratios.—The distribution ratios at 25° of ethylene and propene between carbon tetrachloride and water and between carbon tetrachloride and 1 *N* potassium nitrate are given in Table I. Four or more determinations were made of each value.

TABLE I

DISTRIBUTION RATIOS^a FOR ETHYLENE AND PROPENE AT 25°

Compound	K_w	K_D
Ethylene	33.5 ± 0.4 (0.01-0.02)	40.2 ± 0.3 (0.01-0.02)
Propene	147 ± 1 (0.05-0.09)	225 ± 2 (0.07-0.28)

^a The numbers in parentheses beneath each constant indicate the range of $(B)_0$ used in the determination of the corresponding constant.

Argentation Constants.—The complexes of silver ion with ethylene and propene were studied only at unit ionic strength, with 1 *N* silver nitrate and 0.5 *N* silver nitrate-0.5 *N* potassium nitrate. Six or more determinations were made at the higher silver ion concentration, and at least four

at the lower. The results are summarized in Table II.

TABLE II

ARGENTATION OF ETHYLENE AND PROPENE AT 25° AT UNIT IONIC STRENGTH

Compound	(Agt)	$(B)_0, M$	K_0	K_E
Ethylene	1.000	0.0027-0.0050	2.44 ± 0.01	98.1 ± 1.0
	0.500 ^a	.0019-0.0032	2.28 ± 0.04	91.7 ± 1.7
Propene	1.000	.026-0.073	0.430 ± 0.002	96.8 ± 1.0
	0.500 ^a	.042-0.078	0.409 ± 0.003	92.0 ± 0.7

^a Potassium nitrate was added to maintain $\mu = 1.000$.

The lack of significant variation of the argentation constants with variation in olefin concentration over an approximately twofold range indicates that for ethylene and propene, just as for the other monoolefins studied,¹⁻⁴ there is no significant formation of a di-olefin complex in the concentration range investigated. On the other hand, there is an appreciable decrease in the evaluated constants, K_E and K_0 , with decrease in the silver ion concentration at constant ionic strength. The assumption may be made that $\gamma_{BAg^+}/\gamma_{Ag^+}$ is constant as potassium nitrate replaces silver nitrate; this assumption is convenient,¹⁴ but by no means necessarily correct.⁴ If $\gamma_{BAg^+}/\gamma_{Ag^+}$ is constant, then the variation of K_E (or K_0) with varying concentration of silver ion may be attributed to the formation of a disilver complex, and the corresponding values of K_1 and K_2 (at $\mu = 1$) may be calculated.⁴ The constants obtained in this manner are, for ethylene, $K_1 = 85.3$ and $K_2 = 0.15$; for propene, $K_1 = 87.2$ and $K_2 = 0.11$.

The substitution of the first methyl group on the double bond appears to have essentially no effect on the argentation constant. It seems likely that there are (at least) two opposing effects which approximately cancel here; this matter is discussed in a later paper,¹⁵ in which the relative values of the constants for all of the olefins which have been studied are considered.

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