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The Coördination of Silver Ion with Unsaturated Compounds. III. Mixtures of Trimethylethylene and Cyclohexene

BY H. J. LUCAS, F. W. BILLMEYER, JR., AND D. PRESSMAN

In the preceding paper,[1] it was found that the observed distribution constant of a mixture of *cis-* and *trans*-2-pentene between carbon tetrachloride and water, K_W, and the argentation constant, K_O, agreed well with the value calculated from the individual distribution constants of the 2-pentenes. However, there were marked discrepancies between the observed and calculated values of K_D, the distribution constant of the mixture between carbon tetrachloride and 1 N potassium nitrate solution and of K_E, the argentation constant, which depends on the value and thus the variation of K_D.

TABLE I

DISTRIBUTION CONSTANTS OF TRIMETHYLETHYLENE, T, AND CYCLOHEXENE, C

Temp., 25°; $V_c/V_w = 0.1$

Initial mole fract. N' T	Initial mole fract. N'' C	$(B)_c$ range M	No. of dtns.[a]	N_e'	Observed K_W	Calculated K_W
1.00	0.00	0.93–0.97	3	1.00	2920 ± 30	(2920)
0.75	.25	1.03–1.05	3	0.748	3050 ± 10	3090
.50	.50	0.94–0.94	3	.497	3210 ± 10	3260
.25	.75	.97–1.06	3	.249	3390 ± 20	3410
.00	1.00	.97–0.97	2	.00	3610 ± 10	(3610)
					K_D	K_D
1.00	0.00	1.00–1.02	4	1.00	3460 ± 40	(3460)
0.75	.25	1.01–1.02	6	0.75	3500 ± 20	3720
.50	.50	1.04–1.05	4	.499	3800 ± 20	4010
.25	.75	1.08–1.09	4	.248	4140 ± 10	4360
.00	1.00	1.16–1.18	3	.00	4760 ± 20	(4760)

[a] Each run in duplicate.

In order to test these relationships more extensively, distributions have been made with three mixtures of trimethylethylene and cyclohexene, having 25, 50 and 75 mole per cent. of trimethylethylene. The total concentration of olefin in carbon tetrachloride was kept at 1 M and the silver nitrate solution was 1 N. The method of calculating the equilibrium constants is already described.[1] The data are collected in Tables I and II.

The values of K_W and K_O of mixtures agree well with the calculated values, but those of K_D and K_E do not. In these respects the mixtures of trimethylethylene and cyclohexene resemble the mixture of *cis*-2-pentene and *trans*-2-pentene. With all mixtures where marked deviations take place, the observed values are lower than the calculated ones.

The deviation between observed and calculated values in the case of K_D must be due to some effect of the dissolved salt. It is significant that K_W observed agrees with K_W calculated, indicating that in pure water the presence of one olefin affects to an insignificant extent the activity of the other olefin. But in the potassium nitrate solution this is not true. In the presence of the ions there is some interaction between the two olefins[2] which tends to increase the solubility of one or of both of them in water, thus lowering the value of K_D.

TABLE II

ARGENTATION CONSTANTS OF TRIMETHYLETHYLENE, T, AND CYCLOHEXENE, C

Temp., 25°; $V_c/V_w = 0.2$

Initial mole fract. N' T	Initial mole fract. N'' C	$(B)_c$ M	No. of dtns.[a]	N_e'	K_O Obs.	K_O Calcd.	K_E Obs.	K_E Calcd.
1.00	0.00	0.95	4	1.00	0.00674 ± 0.00019	(0.00674)	23.3 ± 0.8	(23.3)
0.75	.25	.978	2	0.764	.00975 ± .00000	.00965	34.1 ± 0.2	35.8
.50	.50	.977	4	.515	.01276 ± .00013	.01272	48.5 ± 0.7	50.9
.25	.75	1.05	2	.262	.01599 ± .00004	.01586	66.1 ± 1.8	69.1
.00	1.00	1.01	4	.00	.01910 ± .00025	.0910)	91.0 ± 1.3	(91.0)

[a] Each run in duplicate.

The same effect of dissolved salt appears in the observed values of K_E, which are lower than calculated. This effect is not evident in K_O, since the latter constant deals with pentene in the carbon tetrachloride solution, not in the aqueous solution, and the dissolved salt, in this case silver

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[1] H. J. Lucas, R. S. Moore and D. Pressman, THIS JOURNAL, **65**, 227 (1943).

[2] Unpublished work by Mr. F. Hepner in this Laboratory shows that a single olefin (butene) in an aqueous salt solution obeys Henry's law. See also W. F. Eberz, H. J. Welge, D. M. Yost and H. J. Lucas, *ibid.*, **59**, 45 (1937).

nitrate, has no effect on the activity coefficient of the olefin in the carbon tetrachloride solution. Moreover, K_E is complicated further by the necessity of assuming that the salting out effects of silver nitrate on the two olefins are those of potassium nitrate.

The composition of an unknown mixture of trimethylethylene and cyclohexene can be evaluated directly from K_W or from K_O of the mixture, or empirically from K_D or K_E of the mixture. It is probable that a mixture of any two olefins could be analyzed by distribution measurements.

Experimental

Materials.—Trimethylethylene was obtained by the careful fractionation through a seven-foot total reflux column of the amylene prepared by heating *t*-amyl alcohol with oxalic acid[3]; b. p. 38.2–38.3° (760 mm.). The possible small amount of unsymmetrical methylethylethylene which may have been present would not have an appreciable effect on the results. Previous constants,[4] *viz.*, K_D 2165 and K_O 0.00613, are lower than those obtained here.

Cyclohexene was purified by distilling the Eastman Kodak Co. material from sodium in an atmosphere of nitrogen, b. p. 82.1–82.2° (uncor.). It gave a negative test for peroxide on adding potassium iodide, dilute sulfuric acid, and starch. Previous constants,[4] *viz.*, K_D 4305 and K_O 0.0184, are lower than those obtained here.

Carbon tetrachloride solutions approximately 1 *N* in trimethylethylene and cyclohexene were analyzed by bromine absorption. For making up large volumes of the mixtures the proper volume of each to give the desired composition was forced into an especially calibrated pipet[5] by nitrogen, then delivered into a suitable flask filled with nitrogen. The contents were well mixed. Each mixture was used as soon as possible after being made to avoid any change in composition resulting from evaporation.

Distributions.—All distributions were carried out in a thermostat at 25.00 ± 0.05° in an all-glass apparatus equipped with a mercury-sealed stirrer. In the distributions with water and with 1 *N* potassium nitrate the volume of the aqueous phase was 100 to 125 ml. and of the organic phase, 10 to 15 ml. With 1 *N* silver nitrate, these were 50 to 75 ml., and 10 to 15 ml., respectively. After stirring for fifteen minutes in the thermostat, the contents were allowed to stand for one hour, which was sufficient time for the phases to become perfectly clear. Samples were removed by forcing the liquid with nitrogen into calibrated pipets of the type used previously.[5] The carbon tetrachloride sample was 5 ml., and the aqueous sample 150 ml., except when silver ion was present; then 10 to 25 ml. was sufficient.

Analysis.—This was carried out as described previously.

Summary

The distribution constants of mixtures of cyclohexene and trimethylethylene between carbon tetrachloride and water (K_W), and between carbon tetrachloride and 1 *N* potassium nitrate solution (K_D), were determined. Also the argentation constants K_O and K_E were determined. K_W and K_O of the mixtures agree well with the calculated values while K_D and K_E are lower. This is attributed to the fact that in aqueous salt solutions one olefin increases the solubility of the other.

The composition of a mixture of trimethylethylene and cyclohexene, and probably of a mixture of any two olefins may be evaluated empirically from the distribution constant of the mixture between carbon tetrachloride and water, inert salt solution, or silver nitrate solution.

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[3] J. F. Norris and G. Thomson, THIS JOURNAL, 53, 3114 (1931).

[4] S. Winstein and H. J. Lucas, *ibid.*, 60, 836 (1938).

[5] W. F. Eberz and H. J. Lucas, *ibid.*, 56, 1230 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Quaternary Ammonium Phenolates, with Reference to the Claisen Rearrangement

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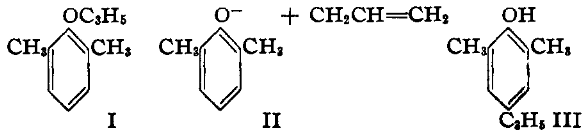
In the rearrangement of allyl aryl ethers such as I to the para position, one of the possible mechanisms involves a dissociation of the ether into a positive allyl ion and a negative phenolate ion as in II. This would be followed by a recombination in the para position, with a shift of a hydrogen atom, to yield the rearrangement product III.[1] It occurred to us that information about these ions as intermediates in the rearrangement might be obtained by a study of allyldimethylphenylammonium phenolates, such as IV. This quaternary ammonium compound


I II III

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[1] For a summary of the evidence, *cf.* (a) Tarbell and Kincaid, THIS JOURNAL, 62, 728 (1940); (b) Tarbell, *Chem. Rev.*, 27, 495 (1940).