The Coordination of Silver Ion with Unsaturated Compounds. II.   *cis*- and *trans*-2-Pentene[1]
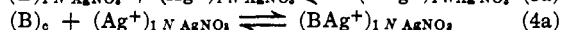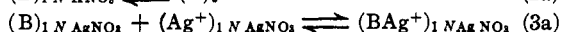
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Since *cis*- and *trans*-2-butene are stable when in contact with aqueous silver nitrate,[1] the determination of the coördination constant of each with silver ion should be possible, and thus the effect of configuration on the coördination reaction could be evaluated. The measurements were carried out on the isomeric 2-pentenes however, since these are liquids, and now are available.[2] The constants of the pure hydrocarbons which were evaluated, K_W, K_D, K_E and K_O, Eqs. 1 to 4, are the respective equilibrium constants for the reactions shown by Eqs. 1a to 4a. Here (B), (Bt) and (Agt) refer to the concentration of the uncomplexed olefin, total olefin and total dissolved silver, respectively, subscript c refers to carbon tetrachloride, w to pure water, and the other subscripts to different salt solutions. The assumption that the complex is composed of one silver ion and one olefin molecule is warranted on the basis of other complexes of this type.[1]

$$K_W = (B)_c/(B)_w \tag{1}$$
$$K_D = (B)_c/(B)_{1\,N\,KNO_3} \tag{2}$$
$$\begin{aligned} K_E &= (BAg^+)_{1\,N\,AgNO_3}/(B)_{1\,N\,AgNO_3}(Ag^+)_{1\,N\,AgNO_3} \\ &= K_D[(Bt) - (B)_c/K_D]/(B)_c[(Agt) - (Bt) + \\ &\qquad\qquad\qquad (B)_c/K_D] \end{aligned} \tag{3}$$
$$\begin{aligned} K_O &= (BAg^+)_{1\,N\,AgNO_3}/(B)_c(Ag^+)_{1\,N\,AgNO_3} \\ &= K_E/K_D \end{aligned} \tag{4}$$
$$(B)_w \rightleftharpoons (B)_c \tag{1a}$$
$$(B)_{1\,N\,KNO_3} \rightleftharpoons (B)_c \tag{2a}$$
$$(B)_{1\,N\,AgNO_3} + (Ag^+)_{1\,N\,AgNO_3} \rightleftharpoons (BAg^+)_{1\,N\,AgNO_3} \tag{3a}$$
$$(B)_c + (Ag^+)_{1\,N\,AgNO_3} \rightleftharpoons (BAg^+)_{1\,N\,AgNO_3} \tag{4a}$$

In calculating K_E (Eq. 3), the use of K_D introduces an uncertainty, for the assumption is made that the activity of the olefin in 1 N silver nitrate is the same as in 1 N potassium nitrate. This uncertainty is eliminated largely in K_O (Eq. 4). Thus K_O is regarded as a better measure of the coördination reaction, for it seems reasonable that the activity coefficients of the olefins in dilute solutions of carbon tetrachloride are alike at similar concentrations. The retention of K_D in Eq. 3 as $(B)_c/K_D$ involves only a second order effect.

When a pure olefin is replaced by a mixture of two olefins, B' and B'' in the distribution measurements, the observed constants K_W, K_D, K_E and K_O in terms of the constants for the individual olefins are expressed by Eqs. 5 to 8.

$$K_W = 1/[N'_c/K'_W + N''_c/K''_W] \tag{5}$$
$$K_D = 1/[N'_c/K'_D + N''_c/K''_D] \tag{6}$$
$$K_E = [N'_c K''_D K'_E + N''_c K'_D K''_E]/[N'_c K''_D + N''_c K'_D] \tag{7}$$
$$K_O = K_E/K_D = N'_c K'_O + N''_c K''_O \tag{8}$$

Here N_e is the mole fraction of a particular olefin in the olefin mixture in the carbon tetrachloride phase at equilibrium. Primed letters refer to B' and double primed letters refer to B''.

The dependence of N'_e on N', the initial mole fraction of B' in the olefin mixture in the carbon tetrachloride phase; on V_c/V_w, the relative volumes of the two phases; and on K' and K'' which are functions of K_W, K_D, or K_O for the individual olefins, is expressed by Eq. 9

$$N'_e = \frac{V_c/V_w + K''}{V_c/V_w + K'' + (V_c/V_w + K')N''/N'} \tag{9}$$

In the distributions with carbon tetrachloride, when the other liquid is pure water, K' is $1/K'_W$; when it is 1 N potassium nitrate, K' is $1/K'_D$; when it is silver nitrate solution K' is K'_O (Ag^+). In the last case the approximation is made that $K'_O = (Bt)/(B)_c(Agt^+)$. Similar constants hold for K''.

In calculating K_W and K_D, the correction for the change in composition of the olefin mixture in the carbon tetrachloride phase due to the extraction process is insignificant. However, the correction is appreciable in the cases of K_E and K_O.

In Table I are the values of K_W, K_D, K_E and K_O determined separately for *cis*-2-pentene, *trans*-2-pentene, and for a mixture the composition of which was *cis*, 25%, *trans*, 75%, calculated from the dielectric constant of the corresponding dibromide.[2,3]

From K_W and K_D it is evident that *cis*-2-pentene is more soluble than the *trans* isomer in water, and from K_E and K_O that the *cis* isomer coördinates better with silver ion. Considering

(1) Original manuscript received December 15, 1941. Preceding paper, S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

(2) H. J. Lucas, M. Schlatter and R. C. Jones, *ibid.*, **63**, 22 (1941).

(3) The cell is the one used previously; H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).

TABLE I

CONSTANTS OF THE ISOMERIC 2-PENTENES: TEMP., 25°; $V_o/V_w = 0.057$

Property	cis-2-Pentene	trans-2-Pentene	Mixture Observed	Mixture Calculated
K_W	2593 ± 24	3320 ± 20	2950 ± 70	3100
N^{cis}	1.00	0.00	0.25	
N_e^{cis}	1.00	0.00	0.247	
No. of runs	3	3	3	
$(B)_c, M$	0.48	0.48	0.45	
K_D	3607 ± 56	5620 ± 140	4096 ± 115	4950
N^{cis}	1.00	0.00	0.25	
N_e^{cis}	1.00	0.00	0.247	
No. of runs	3	3	3	
$(B)_c, M$	0.47	0.49	0.45	
K_E	112.5 ± 1.2	62.2 ± 0.5	65.8 ± 0.0	76.5
K_O	0.0312 ± 0.003	0.0111 ± 0.0001	0.0162 ± 0.0000	0.0152
N^{cis}	1.00	0.00	0.25	
N_e^{cis}	1.00	0.00	0.204	
No. of runs	3	4	3	
$(B)_c, M$	0.31	0.41	0.36	
Dibromide, ϵ	6.51[2]	5.43[2]	5.70	

only K_O, the constant of cis-2-pentene is three times that of trans-2-pentene.

The marked difference in the values of K_O of the two pure hydrocarbons indicates that there is little or no rearrangement or isomerization. This agrees with the observation that no isomerization takes place between the cis and trans isomers of 2-butene while in contact with aqueous silver nitrate.[1] This stability is regarded as a confirmation of the structure previously proposed for complexes of this type,[4] viz., a resonance hybrid of the four forms, I to IV inclusive

I   II

III   IV
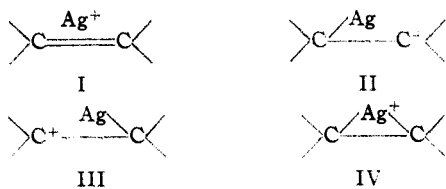
Originally IV was omitted, for it was believed that its contribution was insignificant compared to the other three. However, the stability of the cis and trans complexes seems to indicate a considerable contribution of IV. Keller in his recent review article[5] has pointed out the possibilities in regard to optical isomerism. It is doubtful if any resolution could be realized, however, due to the dynamic nature of the system.

Experimentally determined values of K_W and K_O for the pentene mixture agree well with calculated values while those of K_D and K_E deviate considerably. This suggests that the olefins probably affect each other in the salt solutions.

Considerable preliminary work showed that an apparatus similar to the one used previously[4] was satisfactory when working with 2-butene and with isobutylene, but not with the 2-pentenes. For these it was necessary to use an all-glass apparatus, and to discard rubber stoppers entirely.

Extension of the study of cis–trans effects to ethyl fumarate and ethyl maleate was abandoned when it was found that ethyl fumarate could not be analyzed by a bromine absorption method.

Experimental

Materials.—Carbon tetrachloride was purified[6] and isobutylene,[7] the 2-butene mixture,[8] and the 2-pentene mixture[2,9] were prepared as described previously. The 2-pentene mixture, b. p. 35.5–36.5°, was stored under nitrogen. The pure cis- and trans-2-pentenes were products prepared previously.[2] These had been sealed in an atmosphere of nitrogen and were removed from the ampoules just before the measurements were carried out. The ethyl fumarate and maleate were Eastman products.

Apparatus and Procedure.—The apparatus first used was like the one described previously.[4] The flask, usually 200 ml., immersed in a thermostat at 25 ± 0.03°, was filled with nitrogen, the aqueous phase (1 N potassium nitrate or 1 N silver nitrate), usually 175 ml., and the solution of the unsaturated compound in carbon tetrachloride, usually 10 ml., previously prepared in an atmosphere of nitrogen, were pipetted into the flask and the two phases were stirred mechanically for some time, usually twenty minutes. The phases were allowed to stand quietly for another period, usually sixty minutes, in order to obtain clear solutions. The samples, 2 or 3 ml. of the carbon

(4) H. J. Lucas, F. Hepner and S. Winstein, THIS JOURNAL 61, 3102 (1939).

(5) R. N. Keller, Chem. Rev., 28, 260 (1941).

(6) H. J. Lucas and D. Pressman, Ind. Eng. Chem., Anal. Ed., 10, 140 (1938).

(7) (a) H. J. Lucas and W. F. Eberz, THIS JOURNAL, 56, 460 (1934); (b) C. D. Hurd and L. U. Spence, ibid., 51, 3561 (1929).

(8) R. T. Dillon, W. C. Young and H. J. Lucas, ibid., 52, 1953 (1930).

(9) J. F. Norris and R. Reuter, ibid., 49, 2624 (1927).

tetrachloride phase, 25 ml. of the aqueous phase when silver nitrate was present, 100 ml. of the aqueous phase when it was absent, were forced into the pipets with nitrogen.[4] In the cases of 2-butene and isobutylene satisfactory results were obtained with this apparatus and procedure. But much trouble was experienced with the 2-pentene mixture, because values of different constants varied with standing time, apparently due to absorption of pentene by the rubber stoppers. The apparatus was modified by replacing the rubber stoppers with ground glass joints. This eliminated absorption of pentene by the rubber.

Analysis.—The method of analysis is essentially the one used previously.[1] Although the maximum error in the method is about 2%, most of the determinations are well within this figure.

Only in the absence of oxygen could accurate analyses be realized. In its presence the end-point in the thiosulfate titration is unsatisfactory, for the blue color reappears, the rapidity of reappearance depending upon the amount of peroxide present. Apparently the greater interference from oxygen here, in comparison with earlier work, arises from the fact that the time of standing during the distribution is longer.

Ethyl fumarate could not be analyzed satisfactorily even when mercuric sulfate and acetic acid were added.[6]

Distribution Measurements: Isobutylene.—With the concentration in water, $(B)_w$ ranging from 0.000467 to 0.00119 and the concentration in the carbon tetrachloride phase, $(B)_c$, ranging from 0.264 to 0.692, nine values, 566 to 600 with a mean of 586 $\pm$ 8, were obtained for K_W. There was no indication of a trend of K_W with concentration, or with time of standing, which varied from 5 to 300 minutes. Previously a value of 606 had been obtained, at higher concentrations of isobutylene.[10]

2-Butene Mixture.—Two values for K_D at $(B)_c$ = 0.765 gave an average of 800 $\pm$ 1.5, with respective standing time of one and one-half and three hours. When this was increased to twenty hours, the constant increased to 950, indicating loss through the rubber stopper. Using 800 as the value of K_D against 1 N silver nitrate, the following values were found: 48.7 for K_E and 0.0608 for K_O.

2-Pentene Mixture.—The average of three K_W values obtained in the all-glass apparatus with settling time up to five hours was 2950 $\pm$ 70. The value rose with longer standing time, but much less rapidly than in the apparatus with rubber stoppers. The average of three K_D values was 4096 $\pm$ 115, which checked closely the average of

(10) W. F. Eberz, H. J. Welge, D. M. Yost and H. J. Lucas, THIS JOURNAL **59**, 45 (1937).

three values in the apparatus with rubber stoppers when the settling time was less than two hours, *viz.*, 4040 $\pm$ 100.

The mean of three determinations of K_E in the all-glass apparatus with $(B)_c$ at 0.36 M was 65.8 $\pm$ 0.03, and of six in the apparatus with rubber stoppers 66.9 $\pm$ 0.6 with $(B)_c$ at 0.4 M.

In the all-glass apparatus it was noted that whereas equilibrium was established fairly rapidly when pentene passed from the carbon tetrachloride phase to aqueous silver nitrate (twenty minutes stirring), equilibrium was established so slowly when pentene was being extracted from the aqueous phase by carbon tetrachloride that a stirring time of sixty minutes was insufficient. Presumably this is due to the fact that the concentration of uncomplexed pentene is exceedingly low in aqueous silver nitrate and is restored comparatively slowly by the dissociation of the pentene–silver complex.

cis- **and** *trans*-2-**Pentene.**—With each hydrocarbon three determinations were made of K_W, K_D K_E and K_O. In all cases stirring time was twenty minutes and settling time sixty minutes, in the all-glass apparatus. The values of the constants of the pure hydrocarbons, and of the 2-pentene mixture, are summarized in Table I.

Summary

The distribution constants K_W and K_D of *cis*-2-pentene, *trans*-2-pentene and a 2-pentene mixture between carbon tetrachloride and water and between carbon tetrachloride and 1 N potassium nitrate solution were determined. Also the argentation constants K_O and K_E were determined.

The *cis* configuration is more favorable than the *trans* for solubility in aqueous solutions and also for the coördination reaction.

From the fact that each isomeric 2-pentene has a definite argentation constant it is concluded that no isomerization takes place in the silver complex. This indicates a considerable contribution of the cyclic resonance form to the ground structure of the complex.

The observed values of K_W and K_O for the mixture agree well with those calculated from the constants for the pure components. However, there is considerable deviation between the observed and calculated values of K_D and K_E.