163. *The Estimation of* cyclo*Pentadiene and Indene, and their Polymerisation in Carbon Tetrachloride Solution.*

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Although pure *cyclo*pentadiene and indene polymerise rapidly under ordinary conditions, the rate of polymerisation might be expected to diminish on solution in an inert solvent. The work now described was carried out to see how far this prediction is in accordance with fact, and in the hope that conditions might be found under which the rate of polymerisation is so slow that the rate of interaction of these hydrocarbons with additive reagents such as nitro-compounds could be measured without ambiguity (Hammick and Sixsmith, *J.*, 1935, 580). The first step in the investigation was the working out of a method of analysis which would give a sufficiently rapid and accurate estimate of unimolecular forms present in solutions containing mixtures of monomer and dimer. Such a method was found in a variant of the several analytical processes depending upon the quantitative addition of bromine to unsaturated substances. The use of an acidified solution of potassium bromide and bromate as the source of bromine (Francis, *Ind. Eng. Chem.*, 1926, **18**, 821) is unsatisfactory because acid is known to catalyse polymerisation (Stobbe and Färber, *Ber.*, 1924, **57**, 1838; Schultze, *J. Amer. Chem. Soc.*, 1934, **56**, 1552). We find, however, that dilute solutions (up to about $M/20$) of *cyclo*pentadiene and of indene in carbon tetrachloride absorb accurately and rapidly two atoms of bromine from excess bromine also in carbon tetrachloride. As is shown in the experimental part, the amount of the excess must be controlled (twice the calculated amount) in the case of indene.

With the above technique the estimation of unimolecular indene in presence of its dimer is simple, because, although the latter is unsaturated, its rate of reaction with bromine is very slow (Staudinger, *Helv. Chim. Acta*, 1929, **12**, 934). On the other hand, di*cyclo*pentadiene reacts as rapidly with one molecule of bromine as does *cyclo*pentadiene itself. It is easily shown, however, that if there are a g.-mols. of *cyclo*pentadiene initially present in a litre of solution and if b g.-mols. of dimer are formed, then the number of atoms of bromine that can be absorbed per litre is $2\,(a - b)$.*

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* The concentration of the unimolecular form is $a - 2b$ g.-mols./l.; this reacts with $2(a - 2b)$ g.-atoms of bromine, and b g.-mols. of dimer react with $2b$ g.-atoms of bromine. Hence, the total number of g.-atoms of bromine required for reaction is $2(a - 2b) + 2b = 2(a - b)$.

It has long been known that indene absorbs oxygen (Thiele, *Ber.*, 1900, **33**, 3393), and Davis, Crandall, and Higbee (*Ind. Eng. Chem.*, 1931, **23**, 108) found that the presence of oxygen prevented accurate estimation by the aqueous bromide–bromate method. A similar effect was noticed by Schultze (*loc. cit.*) with *cyclo*pentadiene. We find that solutions of these two hydrocarbons in carbon tetrachloride contain no peroxides when freshly made up with the pure unimolecular forms, negative results being obtained by Kharasch's test (*J. Amer. Chem. Soc.*, 1933, **55**, 2468). On keeping in contact with air, these solutions polymerise slowly, and we have followed the process by titration with bromine. The polymerisation is accompanied by the development of a positive Kharasch test for peroxides. We find, moreover, that the rate of polymerisation is diminished by the progressive addition of the antoxidant acetonitrile to the solutions, becoming zero in acetonitrile itself. The inference to be drawn from these facts is that the polymerisation mechanism involves oxygen. Confirmation of this view comes from the fact that solutions of *cyclo*pentadiene and of indene, prepared and preserved in an atmosphere of nitrogen, do not polymerise. Polymerisation begins, however, after oxygen has entered the systems, its presence being revealed as peroxide.

EXPERIMENTAL.

I. *Experiments with* cyclo*Pentadiene.*—(1) *Preparation of solutions of pure* cyclo*pentadiene.* Pure *cyclo*pentadiene was obtained by the distillation of a commercial specimen, which contained a considerable proportion of di*cyclo*pentadiene. The crude hydrocarbon was placed in a round-bottomed flask fitted with a Dufton-type fractionating column (1 m. long). A stream of dry nitrogen (freed from traces of oxygen by passage, after admixture with 5% of hydrogen, over heated platinised asbestos) was passed for an hour through the apparatus. The hydrocarbon was then distilled slowly in the nitrogen stream, the fraction of b. p. 40—41°/755 mm. being collected. A fitting at the bottom of the condenser enabled the distillate to be collected in either of two receivers, so that the required fraction could be obtained without letting air into the apparatus. Small portions of the fresh distillate were immediately transferred to a tared standard flask (50 c.c.) containing about 25 c.c. of carefully purified and dried carbon tetrachloride. After being weighed, the solutions were made up to 50 c.c. with pure tetrachloride.

Estimation of cyclo*pentadiene in freshly prepared solution in carbon tetrachloride.* The bromine used in the estimations was purified (Cohen, *J. Amer. Chem. Soc.*, 1930, **52**, 2827) by shaking with *N*/10-sodium hydroxide, and distilled from phosphoric oxide in an all-glass apparatus. Solutions were made up in pure carbon tetrachloride (*ca.* *N*/10) and standardised by titration with standard thiosulphate after shaking with potassium iodide solution. 5, 10, or 20 C.c. portions of the *cyclo*pentadiene solutions, prepared as described above, were run (from standardised pipettes) into small conical flasks, and to them various excesses of bromine solution were added. After mixing, the solutions were at once shaken with aqueous potassium iodide, the liberated iodine being titrated with standard thiosulphate (*N*/10 or *N*/100). The figures in Table I show the kind of accuracy attained under the conditions indicated. The first and the last two of the tabulated experiments were carried out with 10 c.c. of solution; the remainder with 5·0 c.c.

TABLE I.

C_5H_6 (g.-mols./l.) ……	0·0395	0·2976	0·0872	0·02976	0·02976	0·01296	0·03420
Br added, as c.c. of *N*/10 ………………	11·05	5·505	4·84	5·505	5·505	6·600	18·60
Excess Br, in terms of *N*/10-$Na_2S_2O_3$, c.c.	7·60	2·57	3·95	2·59	2·62	1·42	4·96
C_5H_6 (g.-mols./l.) found	0·0385	0·02965	0·0872	0·02944	0·02916	0·01295	0·03410

Rate of polymerisation of cyclo*pentadiene in carbon tetrachloride at* 25° : *stabilising effect of acetonitrile.* In Table II are the results of a number of experiments on the rate of polymerisation of *cyclo*pentadiene in carbon tetrachloride, the amount of unimolecular form present at any time t (in hours) being found by reaction with bromine as described above. From the number of g.-atoms of bromine absorbed by aliquot portions of solution, the concentration (in g.-mols./l.) of unimolecular *cyclo*pentadiene present was found by the use of the relation already derived. The velocity constants k were calculated by means of the equation $k = (1/t)x/a(a - x)$, where a is the initial concentration of *cyclo*pentadiene and x is the amount of it polymerised after time t ($x = 2b$, where b is the number of g.-mols. of dimer : see above).

A solution of 0·00872 g.-mols. of *cyclo*pentadiene in pure acetonitrile underwent no alteration in bromine value after keeping for 8 days.

Peroxide formation in cyclo*pentadiene solutions.* The Kharasch test (*loc. cit.*) for peroxides in specimens of unsaturated compounds that have been exposed to air consists in shaking them with a colourless aqueous solution of ferrous ammonium sulphate and ammonium thiocyanate; production of the characteristic ferric thiocyanate coloration shows the presence of peroxide. All solutions of *cyclo*pentadiene in carbon tetrachloride that had been kept for any length of time gave a positive test for peroxide, and a freshly prepared solution (*ca.* 0·1*M*) gave a faint coloration after 15—20 minutes' contact with the air.

TABLE II.

a = 0·02976 g.-mols./l.

Time	16	28	44	53	68
C.c. of *N*/100-Br absorbed by 5·00 c.c.	28·3	27·3	26·6	25·8	25·2
Concn. of diene	0·0269	0·0248	0·0234	0·0218	0·0206
k	0·223	0·238	0·207	0·227	0·219

a = 0·02976 g.-mols./l.: solution contained 1% acetonitrile by vol.

Time	28	52	118	139	169
C.c. of *N*/100-Br absorbed by 4·95 c.c.	28·3	27·4	25·9	25·6	25·8 *
Concn. of diene	0·0274	0·0256	0·0226	0·0216	0·0202
k	0·096	0·105	0·091	0·092	0·091

* Absorbed by 5·13 c.c. of diene solution.

a = 0·02976 g.-mols./l.: solution contained 5% acetonitrile by vol.

Time	5	22	43	118	140
C.c. of *N*/100-Br absorbed by 4·95 c.c.	29·05	28·65	27·35	26·40	25·71
Concn. of diene	28·92	28·14	26·67	23·15	22·12
k	0·083	0·088	0·0895	0·081	0·082

a = 0·03385 g.-mols./l.: solution contained 20% acetonitrile by vol.

Time	50	72	120	147	168
C.c. of *N*/100-Br absorbed by 4·95 c.c.	32·15	31·50	30·40	29·90	28·55
Concn. of diene	31·12	29·80	27·58	26·60	26·10
k	0·052	0·056	0·056	0·055	0·052

We give below the results of an attempt to keep a solution in contact with pure nitrogen for some days. It is seen that after 48 hours oxygen had begun to get in, as shown by a positive peroxide test, although the bromine estimation of hydrocarbon shows no change from the original value. After 70 hours a strong Kharasch reaction was shown and polymerisation had set in.

Time (hours)	0	0·5	24	48	70
Concn. of diene	0·0522	0·0522	0·0523	0·0522	0·0494
Kharasch test	—	—	—	+	++

II. *Experiments with Indene.—Preparation of solutions of pure indene in carbon tetrachloride.* A commercial specimen of indene was distilled twice through a small fractionating column. In the first distillation the fraction of b. p. 178—180° was collected. This was redistilled, and portions of the fraction of b. p. 179—180° were collected in tared flasks. After being weighed, these portions were made up to known volumes with pure carbon tetrachloride.

Estimation of indene in carbon tetrachloride solution. The method used for the estimation of indene was in principle that already described for the estimation of *cyclo*pentadiene; but whereas in the latter case the addition of any convenient excess of bromine in carbon tetrachloride, followed immediately by the estimation of the unreacted bromine, gave satisfactory results, in the case of indene solutions a rather more rigid technique must be followed. It is necessary to have the concentration of the indene to be estimated in the neighbourhood of 0·05 g.-mol./l. (*i.e.*, *ca.* *N*/10), and to add about twice the stoicheiometric amount of bromine in carbon tetrachloride. If the concentration of indene is much above 0·05*M*, more than the theoretical amount of bromine is absorbed; under these conditions some substitution takes place, as is shown by the presence of hydrobromic acid in the solution.

The actual method of estimation consisted in running a known volume of a carbon tetrachloride solution of indene from a standardised pipette into a clean, dry flask and adding pure solvent until the solution was approximately *N*/10 (*M*/20). A measured volume of a standard solution of bromine in carbon tetrachloride was then run in, about 2 equivs. of bromine being added to 1 equiv. of indene. After not longer than half a minute, with shaking, aqueous potassium iodide was added. The iodine liberated after vigorous shaking was estimated with standard (*N*/10) thiosulphate. In Table III are collected results of experiments illustrating the necessity for the technique prescribed above, and the accuracy attained when it is followed.

TABLE III.

Various freshly prepared solutions of indene in carbon tetrachloride were treated with (*a*) slight excess, (*b*) large excess of bromine solution.

C_9H_8 (g.-mols./l.).	Vol. of indene soln., c.c.	Br added, as c.c. of *N*/10.	Excess Br, as *N*/10-$Na_2S_2O_3$, c.c.	C_9H_8 (g.-mols./l.) found.
0·0437	(*a*) 10·0	12·43	4·65	0·0389
	(*b*) 10·0	28·21	19·50	0·0436
0·0450	(*a*) 20·0	19·27	2·32	0·0424
	(*b*) 20·0	34·09	16·06	0·0451
0·0519	(*a*) 10·0	12·7	2·99	0·0485
	(*b*) 10·0	21·45	11·08	0·05185
0·0652	(*a*) 10·0	14·70	2·89	0·05905
	(*b*) 10·0	21·40	8·37	0·06515
0·0778	15·0	41·84	18·05	0·0793

It is seen that, provided a sufficient excess of bromine solution be taken, indene can be estimated satisfactorily in carbon tetrachloride in concentrations up to 0·065*M*.

Effect of concentration on the rate of polymerisation of indene in carbon tetrachloride. The rate of polymerisation of indene in solution is very much slower than that of *cyclo*pentadiene. The results are given below of a series of experiments on the effect of concentration on the rate of polymerisation at 25° in carbon tetrachloride. Owing to the fact that polymerised indene reacts only very slowly with bromine, the actual amount of free indene in partially polymerised specimens is obtained directly from the results of titrations carried out after dilution, as described above.

C_9H_8 (g.-mols./l.) initially	0·0519	0·1000	0·4999	0·657	1·500	2·415
% polymerised in 24 hours	nil	nil	0·48	0·60	1·2	6·0

Peroxide effect in indene solutions : solutions made up in absence of air. All indene solutions made up as hitherto described showed the presence of peroxide when tested by Kharasch's method (*loc. cit.*). Solutions of indene in carbon tetrachloride were therefore made up in oxygen-free nitrogen with indene freshly distilled in pure nitrogen. Indene and carbon tetrachloride were distilled into a storage flask in the nitrogen, which was used to force out portions of the solution when required for analysis. The storage flask was not completely air-tight, as is shown by the results given in Table IV, where it is seen that after 90 hours sufficient oxygen had got in to give a positive test for peroxide; measurable change in the bromine titration value was not detectable until the next day. Data are added to show the behaviour of a solution made up in nitrogen as above but kept in contact with air.

TABLE IV.

	Stored in nitrogen.						In contact with air.		
Time (hours)	0	22	47	66	90	120	0	1·25	23
C_9H_8 (g.-mols./l.) ...	3·615	3·620	3·620	3·615	3·610	3·450	1·230	1·230	1·190
Peroxide test	—	—	—	—	+	++	—	+	++

Solutions of indene in pure acetonitrile (up to 4*M*) did not polymerise by more than 1% on keeping in stoppered bottles in contact with air for periods up to 14 days.

SUMMARY AND CONCLUSIONS.

It has been found (i) that *cyclo*pentadiene and indene can be estimated when diluted in carbon tetrachloride to an accuracy of 2—3% by the addition of bromine, also in carbon tetrachloride; (ii) that the polymerisation of *cyclo*pentadiene in carbon tetrachloride follows a bimolecular law, and that the polymerisation of indene under the same conditions is a much slower process; (iii) that the rate of polymerisation of each of these hydrocarbons in carbon tetrachloride is diminished by the addition of the antoxidant acetonitrile, and that no appreciable polymerisation occurs in pure acetonitrile, or in carbon tetrachloride when oxygen is excluded. It appears that polymerisation is connected with the formation of peroxide in the solutions of the hydrocarbons. It is therefore highly probable that the polymerisations of *cyclo*pentadiene and indene are processes involving autoxidation, analogous to those known to occur in the case of acraldehyde and other similar substances (Moureu and Dufraisse, *Compt. rend.*, 1922, **174**, 258 : for other cases of autoxidational condensation, see " Considérations sur l'autoxydation," Institut international de chimie Solvay, 1926).

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