515. *The Interaction of Aluminium Bromide with Olefins and with Benzene.*

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Vapour-pressure measurements have been made of solutions of aluminium bromide in *cis/trans*-pent-2-ene and in pure *cis*-pent-2-ene. These indicate that in concentrated solution the solute is present as a weakly solvated dimer, Al_2Br_6, which undergoes partial dissociation on dilution. No solid complex is formed at 0°, the phase separating from concentrated solution being crystalline Al_2Br_6. In contrast, aluminium bromide separates from benzene solution as $Al_2Br_6,2C_6H_6$ which has a different type of crystal lattice.

Ultraviolet absorption measurements of aluminium bromide in benzene show an absorption below about 2800 Å which does not obey Beer's law and of which only the absorption edge can be observed. Pent-2-ene solutions also show an intense absorption in the same region.

MANY studies have been made of the interaction of aluminium bromide with benzene and other aromatic hydrocarbons but none hitherto successfully with olefins, at all events in the absence of a third component. Considerable interest, however, attaches to this question in view of the wide use of olefins in conjunction with aluminium halides in a variety of reactions. There are recorded in the literature a number of complexes between aluminium halides and olefins, but an examination of these reports shows that in every case a third component, usually water or hydrogen halide, was also present.

It might reasonably be expected that some complex formation might occur between aluminium bromide and an olefin, since the first is a Lewis acid and the second a Lewis base. In fact, in some respects olefins appear to be more basic than benzene, *e.g.*, in their behaviour towards iodine.[1] On the other hand, Chatt[2] has produced much experimental evidence to show that a stable metal–olefin bond is only to be expected when *d*-electrons from the metal atom also can contribute to the bond formation.

Several years ago we sought to examine this question by phase studies, but the selection of a liquid olefin with a measurable vapour pressure between 0° and room temperature and sufficiently stable in the presence of aluminium bromide proved very difficult. Most olefins, even when well dried by usual standards, rapidly polymerise in the presence of aluminium bromide. It was found, however, that pent-2-ene was reasonably stable, especially after several pre-treatments with aluminium bromide, and a number of phase studies were carried out in this solvent at about 18°·[3] these gave no evidence of solid complex formation.

We have now extended this work and obtained solutions of aluminium bromide in pent-2-ene which were stable for several weeks. We have also examined the ultraviolet absorption of these solutions and have re-examined that of solutions of aluminium bromide in benzene, which was studied by Eley and King[4] under somewhat different conditions.

EXPERIMENTAL

Pent-2-ene.—Commercial pent-2-ene was boiled with sodium wire and fractionated twice through a Fenske column; it had b. p. 36—37°/759 mm. This is designated below as " pent-2-ene." Infrared absorption showed that it consisted mainly of the *cis*- and the *trans*-isomer in roughly equal amounts, together with traces of other unidentified compounds. In the later experiments we were able, through the courtesy of the Polymer Corporation of Canada, to use a sample of pure *cis*-pent-2-ene (95 moles % minimum). This also was dried with sodium wire and fractionally distilled, then having b. p. 36·5° ± 0·1°/747 mm., and is designated below as " *cis*-pent-2-ene."

Benzene.—" AnalaR " benzene was fractionally frozen three times to remove homologues, kept for several months over phosphoric oxide, and fractionated; it had b. p. 80·1°/762 mm.

Aluminium Bromide.—This was prepared from the elements, purified by three or four vacuum-sublimations, and stored in the usual fragile hook-ended ampoules. *X*-Ray examination of the solid phases was carried out by shaking some of the solid, with the aid of small glass balls, into a Pyrex capillary tube sealed on to the apparatus, and photographing it in a 19-cm. camera with filtered Cu-K_α radiation.

Vapour-pressure measurements were made, in an all-glass sealed apparatus, of solutions of aluminium bromide in pent-2-ene at 0° and −23° and in pure *cis*-pent-2-ene at 0°. Typical runs in pent-2-ene are shown in Fig. 1. On first condensation of the purified commercial pent-2-ene on to the aluminium bromide, heat was evolved and the bromide dissolved to give a yellow solution from which about 70% of the pent-2-ene could be vapourised off; the rest had clearly polymerised. On distillation (by condensation *in vacuo* at −195°) of the unpolymerised pent-2-ene on to a fresh amount of aluminium bromide and warming to 0°, much less polymerisation occurred and the colour was paler. After four such pre-treatments with aluminium bromide a colourless solution was obtained which was quite stable. The pure *cis*-pent-2-ene gave a stable colourless solution after only one pre-treatment with aluminium bromide. This suggests that the aluminium bromide removed from the purified commercial pent-2-ene, not only residual moisture but also traces of polymerisable impurities.

Vapour-pressure–composition curves at 0° showed only one ill-defined break at about 5—6 moles of pent-2-ene per mole of Al_2Br_6, where a white solid separated. Chemical analysis and *X*-ray examination of this solid, which had risen to room temperature in the meantime, showed that it was crystalline aluminium bromide. The solubility at −23° being much smaller, solid phase was present throughout the measurements. At both temperatures the pressure fell off with removal of solvent with no evidence of solid complex formation, the only solid phase separated being the crystalline dimer Al_2Br_6. On the other hand, the high solubility of the aluminium bromide, and the abnormal depression of vapour pressure in the more concentrated

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[1] Fairbrother, *J.*, 1948, 1051.

[2] Chatt, *J.*, 1949, 3340; Chatt and Duncanson, *J.*, 1953, 2939.

[3] Kidd, M.Sc. Thesis, Manchester, 1951.

[4] Eley and King, *J.*, 1952, 4972.

solutions, point to the existence of some kind of weak association between the dimer and the olefin in these solutions. In all cases almost the whole of the olefin could be recovered from the solutions and proved to be isomerically unchanged.

Calculations were made of the apparent molecular weight of the solute, from the lowering of the vapour pressure, in both pent-2-ene and *cis*-pent-2-ene solutions. The individual molecular weights showed some degree of scatter about a smooth curve (Fig. 2), approaching a value somewhat less than that of the dimer in the more concentrated solutions, falling off to values approaching that of the monomer in solutions containing about 10% mole-fraction of Al_2Br_6. This again is consistent with a weak solvent–dimer association and with a dissociation into the monomer in dilute solution.

FIG. 1.

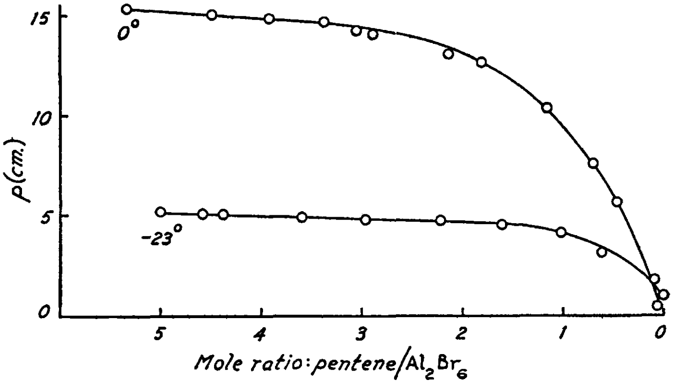
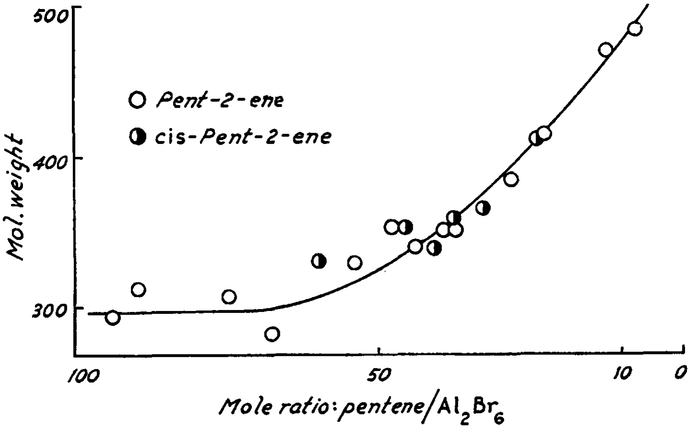


FIG. 2.



A number of other olefins were examined in the same way, *viz.*, *cyclo*hexene, trimethylethylene, *cyclo*pentadiene, and di*iso*butene, but in none of these was it found possible to check the polymerisation so completely as in pent-2-ene. Such measurements as were made, however, gave no evidence of the formation of a solid complex.

A small amount of dry hydrogen bromide was condensed into a cooled colourless solution in pent-2-ene. On warming to room temperature the solution quickly polymerised to a deep yellow viscous oil from which no pent-2-ene could be recovered.

Ultraviolet Absorption Measurements.—Eley and King[4] examined the ultraviolet absorption of benzene solutions of aluminium bromide, following a suggestion by Hildebrand that it might be possible to demonstrate the formation of a complex between the two, along the line pursued by Benesi and Hildebrand for benzene and iodine.[5] These authors found an intense absorption peak at 2970 Å, which may be ascribed to an iodine–benzene complex. Eley and King reported

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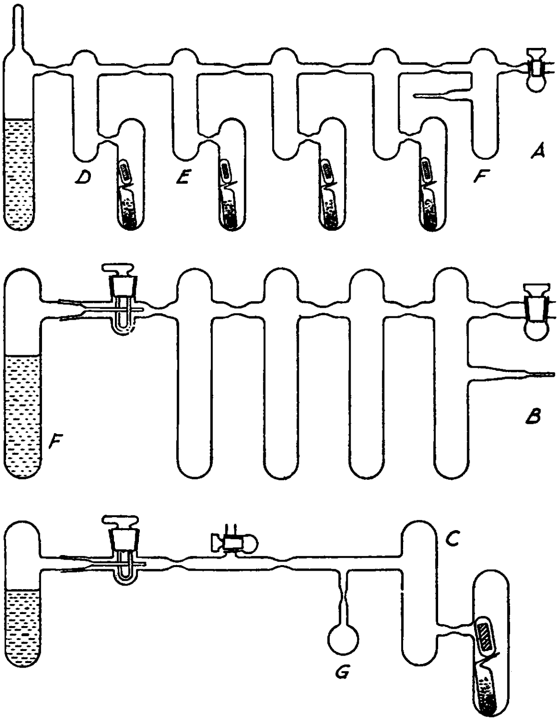
[5] Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

an absorption band of aluminium bromide in benzene at 2785 Å which they attributed to a charge-transfer spectrum of a complex, *i.e.*, for the transition $C_6H_6,Al_2Br_6 \longrightarrow C_6H_6^+,Al_2Br_6^-$. Since, about the same time, other authors[6] reported that olefins and chlorinated olefins gave iodine solutions which showed the presence of ultraviolet bands matching those in aromatic hydrocarbons, it seemed desirable to examine the ultraviolet absorption of aluminium bromide in pent-2-ene. Further, it was decided to repeat Eley and King's measurements under different conditions, since the existence of these bands has been called into question by Evans's observations[7] on the absorption by diphenyl measured in benzene solution.

It has been pointed out by several workers that spurious absorption maxima may be observed in solution spectra measured with modern photoelectric spectrophotometers having only a single monochromator, and whilst attention has been chiefly directed towards such spurious maxima at very short wavelengths (<2300 Å), probably largely owing to stray radiation, Evans[7] has pointed out that spurious maxima may also occur at much longer wavelengths, in a region where the solvent itself also starts to absorb. The absorption by solutions of aluminium bromide in benzene and in pent-2-ene has therefore been measured in several ways. Evans's advice that, when using a solvent which itself absorbs, one should use very thin cells or dilute with a non-absorbing solvent, is not applicable in the present instance. The absorption disappears if one dilutes the solution with *cyclo*hexane, whilst the construction of very thin all-quartz completely sealed cells is difficult and these were not obtainable. All the present measurements were made in 5-mm. cells, with the pure solvent in a similar comparison cell.

FIG. 3.



The solutions were made in the apparatus shown in Fig. 3. In the pre-treatment line *A*, which was also used for the final drying of the solvents used in the vapour-pressure measurements, the purified solvent was condensed in a vacuum at −195° on to freshly sublimed aluminium bromide in *D*, allowed to melt, and condensed on to more aluminium bromide in the next tube *E*, and so on to *F*. The dried solvent was then transferred to line *B* in which it was subjected to four further fractionations *in vacuo*, and finally to *C* in which it was condensed

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[6] Freed and Sancier, *J. Amer. Chem. Soc.*, 1952, **74**, 1273; Ketelaar and van de Stolpe, *Rec. Trav. chim.*, 1952, **71**, 805.

[7] Evans, *Chem. and Ind.*, 1953, 1061.

on to a weighed amount of pure Al_2Br_6 and the solution transferred by tilting the apparatus into the 5-mm. quartz cell *G*. This was joined to the rest of the apparatus by a graded quartz–Pyrex seal and sealed off after filling.

The absorption was measured with a Unicam S.P.500 spectrophotometer, a standard Beckman D.U., and a Beckman D.U. spectrophotometer which had been fitted with a photomultiplier, increasing its sensitivity by a factor of 100 and enabling much narrower slits to be used. With these instruments, evidence was obtained of an absorption band in benzene–aluminium bromide solutions at approximately the same, or at slightly shorter wavelengths, as reported by Eley and King (Fig. 4). Photographic examination of the spectra, however, with a Spekker photometer and Hilger medium quartz spectrograph, failed to reveal a maximum in the absorption, which increased continuously into the region where the benzene begins to absorb. Although, however, an apparent maximum absorption between 2750 and 2800 Å, indicating the presence of an absorption band in this region, may be spurious and due to instrumental errors, there is no doubt whatever that the addition of aluminium bromide to benzene gives rise to a new chemical species which absorbs strongly in the ultraviolet. This was most simply demonstrated by photographing the emission from a 2 kVA water-cooled hydrogen lamp, by means of the Hilger medium quartz spectrograph, through (*a*) a solution of aluminium bromide in pure *cyclo*hexane, (*b*) pure benzene, and (*c*) a solution of aluminium bromide in benzene containing 0·080 mole per litre. Solution (*a*) was quite transparent down to about 2250 Å, (*b*) began to show appreciable absorption at about 2740 Å, whilst (*c*) began to show absorption just below 3000 Å; by 2800 Å, where the benzene alone was showing no absorption, this had become very intense, and is clear evidence of the formation of some new complex in these solutions. The inability of Eley and King to obtain an initially optically clear solution of aluminium bromide in *cyclo*hexane must be attributed to minute traces of water still remaining in the solvent, which are difficult to remove except by the present method using aluminium bromide. This gave solutions without any trace of cloudiness.

The absence of an observable maximum makes it very difficult to draw precise quantitative conclusions about the relation between the absorption and the concentration of absorbing species. Nevertheless, by comparing the absorption of a series of solutions, at, say, 2800 Å, well on the long-wave side of the benzene absorption, where instrumental errors of the kind discussed may be considered to be negligible, it appears that the absorption does not follow Beer's law, but that the molar extinction increases upon dilution, roughly linearly with the concentration. These results also are consistent with the view that aluminium bromide, weakly solvated as the dimer, Al_2Br_6, in concentrated solution, dissociates to a small extent into the momomer $AlBr_3$, upon dilution. The solvation of the dimer is fairly weak and the solvate probably does not contribute much to the absorption under discussion: in fact, Brown and Wallace[8] found that molecular weights calculated from the lowering of the vapour pressure in benzene solution pointed to the existence of the aluminium bromide, in such solutions, primarily as the unsolvated dimer with relatively little tendency towards dissociation into the monomer.

On concentration of benzene solutions, however, the solid phase which separates, and which several workers have shown to have the composition $Al_2Br_6,2C_6H_6$ or $AlBr_3,C_6H_6$, with an incongruent m. p. of 37°,[9] is a definite solvate. *X*-Ray diffraction by this solid showed that it has a crystal lattice quite different from that of aluminium bromide. It crystallises in large, thin, birefringent plates. The extinction is oblique and the crystals are probably triclinic. The quality of the *X*-ray photographs left much to be desired: a heavy background scattering was present, probably caused in part by the concentrated mother-liquor accompanying the crystals, and a slight " spottiness " due to lack of control over the crystal size. Nevertheless, the following lines could be measured, which confirm that the crystal symmetry is low, and not cubic as suggested by Plotnikov and Gratsianskii.[9] A number of other lines, weaker and less well defined, were also present.

d/*n* (Å)	1·90 w	1·98 vw	2·57 vw	2·94 m	3·00 m	3·07 w	3·17 s	3·26 s
	3·35 w	3·46 s	4·14 m	4·73 w	4·98 w	6·08 m	6·73 m	

Whether this is a definite compound or a crystalline solvate is still an open question: the latter, however, seems the more probable. In either event the aluminium bromide appears to be present as the dimer.

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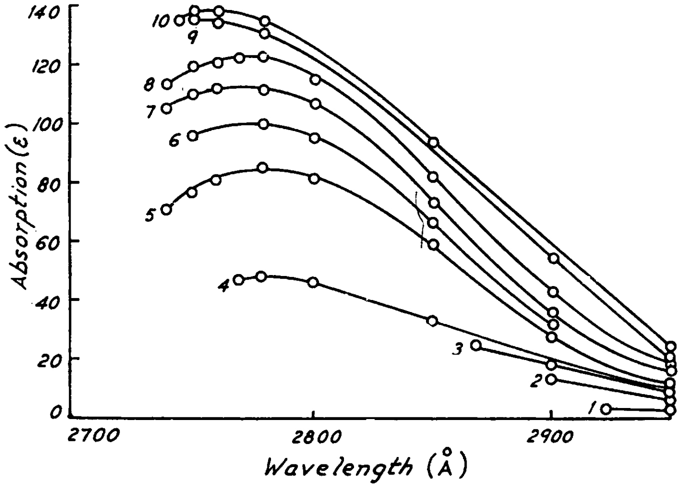
[8] Brown and Wallace, *J. Amer. Chem. Soc.*, 1953, **75**, 62.

[9] Plotnikov and Gratsianskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1947, 101; *Chem. Abs.*, 1939, **33**, 2432; 1948, **42**, 4480; Eley and King, *Trans. Faraday Soc.*, 1951, **47**, 1287; Van Dyke, *J. Amer. Chem. Soc.*, 1950, **72**, 3619.

Additional evidence that aluminium bromide is present in concentrated solution essentially as the dimer, which undergoes dissociation on dilution, is given by recent experiments by Dallinga at the Koninklijke/Shell Laboratorium.[10] In the first place, *X*-ray diffraction of a concentrated solution of aluminium bromide in benzene gave a picture of two distorted tetrahedra corresponding to that given by electron-diffraction measurements on the vapour,[11] and, secondly, measurements of the dipole moment of aluminium bromide in benzene, in the 1-cm. range and in very dilute solution under rigorously dry conditions, gave a value of ~5 D. This may be compared with Nespital's dipole measurements[12] made at a lower frequency (~80 m.). These results, when extrapolated to infinite dilution, also give a value of ~5 D for the moment of aluminium bromide in benzene. In contrast, Nespital obtained a value of 2·5 D for aluminium iodide in benzene, and Eley and King reported that solubility measurements gave no indication of solid complex formation in this system. In confirmation of this different behaviour of aluminium iodide, we have also found, during the present work, that the *X*-ray powder photograph of the solid deposited from a benzene solution of aluminium iodide was identical with that of crystalline aluminium iodide itself.

FIG. 4.



Moles of Al_2Br_6 per l.: (1) 0·618, (2) 0·227, (3) 0·136, (4) 0·0449, (5) 0·0439, (6) 0·0383, (7) 0·0221, (8) 0·0189, (9) 0·0103, (10) 0·0090.

A smaller number of ultraviolet absorption measurements were carried out on solutions of aluminium bromide in pent-2-ene and in pure *cis*-pent-2-ene. These gave the same overall picture as in benzene, namely, the observation of an absorption " edge " at a somewhat shorter wavelength than in benzene, at about 2700 Å, any maximum absorption being beyond the range of the instruments. Photography of the continuous hydrogen spectrum through the solutions, however, gave much clearer evidence of complex formation than in the case of benzene, since the beginning of the absorption by the solution was much more widely separated from that of the solvent. Whereas the pure *cis*-pent-2-ene showed only the beginning of an absorption at about 2400 Å, a solution of aluminium bromide containing 0·0171 mole per litre began to absorb at wavelengths above 2700 Å, and by 2680 Å the absorption was too dense to be measured. Examination of the absorption edge by the photoelectric instruments showed that here also the absorption did not obey Beer's law.

We are indebted to Messrs. Imperial Chemical Industries Limited for the loan of the *X*-ray camera.

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[10] Dallinga, I.U.P.A.C. Abs. 1953, 172; Proc. Symp. on Co-ordination Chemistry, Danish Chem. Soc., 1954, 134; and personal communication.

[11] Palmer and Elliott, *J. Amer. Chem. Soc.*, 1938, **60**, 1852.

[12] Nespital, *Z. phys. Chem.*, 1932, *B*, **16**, 153.