CCCLXXXI.—*Orientation in the Addition of Halogens and Hydrogen Halides to Simple Ethylene Derivatives. Part II. Addition of Hydrogen Halides to Propylene and* n-Δ^{α}-*Amylene.*

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ALTHOUGH suggestions have already been made (Burton and Ingold, J., 1928, 912; compare Bennett, *Ann. Reports*, 1929, **26**, 121; Farmer, *ibid.*, 1930, **27**, 87) with regard to the mechanism of the influence of solvents on orientation in the additions of halogens and halogen hydrides to conjugated unsaturated systems, the considerations hitherto advanced have been concerned solely with effects relating to the direction taken by the final stage of reaction. It is obvious, however, that any general treatment of this side of the subject of conjugative additions must take account also of the effect of solvents on the orientation of the point of incidence of reaction. It was after a preliminary consideration of the principles which might be expected to operate in this connexion that we decided, before proceeding further, to control our views by envisaging their application in the more elementary problem of orientation in additions to singly unsaturated systems. We discuss in this paper only the comparatively simple case of the addition of hydrogen halides to olefins of the type $R{\cdot}CH{:}CH_2$, where R is an alkyl group.

The group R, acting in the direction of the residue $\cdot CH{:}CH_2$, is considered to repel electrons. In so far as this effect travels through the molecule, it must lead to the orientation $R{\cdot}CH(X){\cdot}CH_2(H)$ and should be but little influenced by the medium.

The group R, acting also in the general direction of the residue $\cdot CH{:}CH_2$, but outside the molecule itself, is likewise considered to repel electrons, anions, and the negative ends of polarised molecules, and to attract protons,* kations, and the positive ends of polarised molecules. This effect must tend to orient the addendum in the sense of the expression $R{\cdot}CH(H){\cdot}CH_2(X)$, and since it travels through the medium, it must be profoundly affected by the nature of the medium.

It is quite clear that this second effect should be strongest in gas reactions, weaker in non-polar solvents, and very weak in strongly polar solvents; but a more precise relationship between the magnitude of the influence and the nature of the solvent is difficult to define. If the group R were at a comparatively large distance, *e.g.*, 100 Å.U., from the point at which its effect is being considered, the matter would be simple: we could take the dielectric constant of the solvent (or its equivalent in terms of the electric moment and distortion coefficient of the solvent molecules) as the measure of the influence of the medium on the externally propagated polar field. But at the short distances with which we are concerned other electrical phenomena enter the problem, namely, electrical saturation effects, including influences due to electrostriction and molecular and field anisotropy, and the interactions of quadrupoles and higher multipoles with one another and with dipoles, and to distortion effects; the statistical calculation of these combined influences is at present impossible. It is true that all these component forces together contribute to the internal pressures of liquids but so also does the effect of quantum-mechanical reciprocal perturbations, which (so far as we have been able to follow the application of perturbation-theory to our problem) would not contribute to a proportional extent to

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* Except that very near the surface of R it may be overlaid by selectivity in the van der Waals forces.

the influence of solvents on the orienting molecular field.* Thus the dielectric constant takes count of too little and the internal pressure of too much, and a rough correlation with orientation is the most that can be expected from either property; up to the present we have not been able to think of a macrophysical quantity which should provide a true measure of the local electrical susceptibility of a solvent. Where, however, two solvents differ *very widely*, and in the *same sense*, with regard to both their dielectric constants and their internal pressures, it should be possible, we think, to predict with moderate certainty their relative effects on orientation in addition.

The effect of the medium on the additive reagent itself has also to be considered. Reagents such as hydrogen halides, which add in the molecular form and have greater chemical activity as molecules than as ions, will be deactivated in an environment characterised by high electrical susceptibility, and under these conditions might select the more exclusively for attack those positions in which the electron availability is highest. In the cases with which we are now concerned this medium-effect would collaborate with that discussed above, and to that extent theoretical expectation regarding the direction and relative magnitude of the influence of solvents on orientation is simplified.

There are a number of scattered observations in the literature (compare, for instance, Michael and Zeidler, *Annalen*, 1911, **385**, 265; Ipatief and Ogonowski, *Ber.*, 1903, **36**, 1988) indicating a medium-effect on orientation in the addition of hydrogen halides to *as*-alkylated ethylenes; but in the record of these experiments some essential datum (usually concentration, the importance of which is shown below) is omitted, and it is therefore scarcely possible, on the basis of known results, to make any more precise deduction than that a medium-effect exists.

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* If it were not for the quantum-mechanical effect, the reflection that, for the microphysical problem of reaction in solution, a complex of molecular electric quantities, which together contribute to internal pressure, must take the place occupied by the dielectric constant in macrophysical relations would possibly furnish a physical basis for the cohesion principle of Richardson and Soper (J., 1929, 1873); for a reaction in which the cohesion of the products is greater than that of the factors must involve a *net* separation of charges—a resultant opening of molecular field forces—and it should therefore be assisted by those electrical conditions (high local electrical susceptibility) which make for a high internal pressure (high cohesion), just as the separation of a pair of oppositely charged plates would be assisted by a medium of high dielectric constant in the macrophysical case. Probably the quantum-mechanical effect on cohesion is to be blamed for the circumstance that the Richardson–Soper relation is only rough, and for the fact that the various measures of cohesion which have been proposed from time to time do not precisely agree with one another.

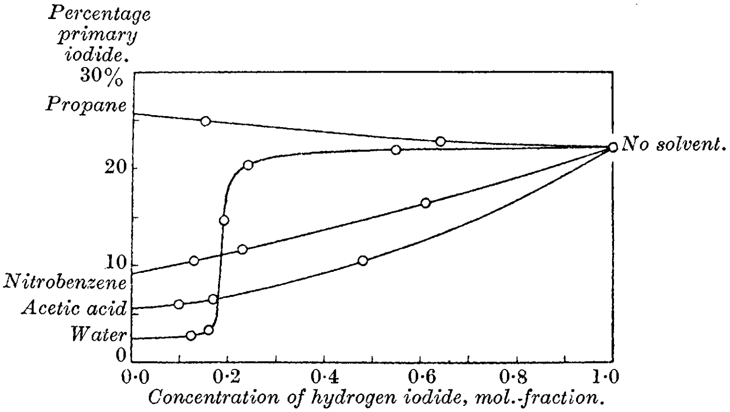
We have studied the addition of hydrogen iodide to propylene, and the addition of hydrogen bromide and of hydrogen iodide to n-Δ^{α}-amylene. It will be sufficient to refer here to the most fully investigated reaction, namely, the addition of hydrogen iodide to propylene.

Propane, acetic acid, nitrobenzene, and water were employed as solvents, light being excluded in all cases. The preceding discussion makes it clear that, whilst *iso*propyl iodide should be the main product, the proportion of n-propyl iodide formed by addition in dilute solution should be highest in propane and lowest in water. This is so.

The dielectric constants [*] of the four solvents place them in the following order :

Propane (1·8) < *Acetic acid* (7·1) < *Nitrobenzene* (36) < *Water* (80)

Addition of hydrogen iodide to propylene in various solvents.



whereas their internal pressures [†] place them in a different order, namely :

Propane (0·56) < *Nitrobenzene* (1·07) < *Acetic acid* (1·95) < *Water* (4·60).

Their relative effects on the orientation of the addition reaction in dilute solution correspond to the second of these series.

The connexion between the orientation and the nature of the solvent and concentration of the solution, so far as we have traced these relations, is exhibited on the accompanying diagram.

The special form of the curve for water is possibly explicable by the circumstance that, whilst the other solutions remain homo-

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[*] The assumed dielectric constant for liquid propane is based on the known values for pentane and its higher homologues.

[†] The figures are relative values due to Mortimer (*J. Amer. Chem. Soc.*, 1923, **45**, 633), the recorded value for hexane being adopted for liquid propane.

geneous, the aqueous solutions separate into two phases at an early stage of dilution. One can well imagine that, with progressive dilution, the reaction would be retained in the hydrocarbon layer until the quantity of water was sufficient to strip practically the whole of the hydrogen iodide from that phase, and only then would the reaction pass into the aqueous phase; on this basis the upper portion of the water curve should be asymptotic to the curve appropriate to a hydrocarbon solvent, whilst the lower portion should be asymptotic to the true water curve.

EXPERIMENTAL.

Materials.—Hydrogen bromide, generated by dropping concentrated hydrobromic acid on to phosphoric oxide, was passed over moist red phosphorus, through a vessel at − 35°, over phosphoric oxide, and then either into a strong-walled tube cooled in liquid air, or into a solvent, or into a previously prepared solution of known strength according to the requirements of the experiment.

Hydrogen iodide, generated analogously with precautions against the access of atmospheric oxygen and light, was passed over moist red phosphorus, through a concentrated solution of calcium iodide, over phosphoric oxide, and either into a tube surrounded by liquid air, or into a solvent, or into a solution of known concentration.

Propylene was prepared from *iso*propyl alcohol and syrupy phosphoric acid. Dried and fractionated, it had b. p. − 49° to − 47°.

n-Δ^{α}-Amylene was prepared from *n*-amyltrimethylammonium iodide, *via* the hydroxide. It was washed with acid and water, dried, and distilled. Our b. p., 29—31°, does not agree with that recorded by Brochet (39—40°; *Bull. Soc. chim.*, 1892, **7**, 567), by von Braun (39—40°; *Annalen*, 1911, **382**, 19), and by Norris and Joubert (39—40°; *J. Amer. Chem. Soc.*, 1927, **49**, 873), notwithstanding that von Braun used the same method of preparation as that employed by ourselves. It agrees moderately well, however, with the b. p. given by Kirrmann (30·5—31°; *Bull. Soc. chim.*, 1926, **39**, 988) and by Bougel (32·5°; *ibid.*, 1927, **41**, 1475), and exactly with the most recent record, namely, that of Dykstre, Lewis, and Boord (29—31°; *J. Amer. Chem. Soc.*, 1930, **52**, 3396).

Propane, prepared from *n*-propyl iodide by the Grignard reaction, had b. p. − 44° to − 42°. Acetic acid was purified by freezing, and nitrobenzene by distillation.

The *n*-propyl iodide required for the refractometric analyses was prepared by Norris's method (*Amer. Chem. J.*, 1907, **38**, 640) from carefully fractionated samples of *n*-propyl alcohol of different origins. The iodide was washed thrice with water, thrice with sodium hydrogen carbonate, once with sodium hydrogen sulphite, and thrice with water. It was dried with calcium chloride and distilled until the refractive index remained constant. The refractive indices of several samples prepared in this way were not quite the same, and the specimens were therefore washed successively with calcium chloride solution, sulphuric acid, sodium hydrogen sulphite and water, and were again dried and distilled in oxygen-free nitrogen in the dark. They then had the same refractive index, $n_{5461}^{15\cdot0^\circ}$ 1·51249.

*iso*Propyl iodide was prepared by Norris's method (*loc. cit.*) from carefully fractionated samples of *iso*propyl alcohol of various origins. The products were washed successively with water, sodium hydrogen carbonate, sodium hydrogen sulphite and water, and were dried with calcium chloride and distilled in the absence of light and oxygen. Their indices of refraction were identical, $n_{5461}^{15\cdot0^\circ}$ 1·50419.

n-Amyl iodide (α-iodo-*n*-pentane), prepared from the alcohol with analogous precautions, had b. p. 153—155°/756 mm., $n_{5461}^{15\cdot0^\circ}$ 1·49060.

sec.-n-Amyl iodide (β-iodo-*n*-pentane), obtained from a single sample of *sec.-n*-amyl alcohol prepared by ourselves, had b. p. 142—144°/748 mm., $n_{5461}^{15\cdot0^\circ}$ 1·50140.

n-Amyl bromide (α-bromo-*n*-pentane), obtained from the alcohol and hydrobromic acid, had b. p. 126—128°/756 mm., $n_{5461}^{15\cdot0^\circ}$ 1·43603.

sec.-n-Amyl bromide (β-bromo-*n*-pentane), prepared analogously from our own alcohol, had b. p. 114°/748 mm., $n_{5461}^{15\cdot0^\circ}$ 1·44945.

Method.—When the solution of hydrogen halide could not be prepared, or when its concentration could not be accurately adjusted at the ordinary temperature, the reagent and the solvent were separately introduced into the thick-walled reaction-tube at the temperature of liquid air. The olefin was enclosed in a comparatively thin-walled tube which was introduced into the reaction-tube before the latter was sealed. The materials having attained the ordinary temperature, the reaction tube, enclosed in a brass tube to exclude light and as a precaution in case of bursting, was shaken in order to break the inner tube containing the olefin, and then left (on a shaking machine in the experiments with aqueous solutions) for the requisite period (1—50 days). The product was isolated by methods which varied according to the nature of the solvent, and was distilled to constant refractive index with precautions analogous to those used in the preparation of the reference halides. A Pulfrich instrument, and the green line of the mercury arc spectrum, were used for the refractometric analyses, differences of refractive index being read directly on the drum; a linear mixture law was assumed in calculating the compositions of the mixtures of isomeric halides. In the experiments with propylene the analytical error is estimated as 0·3%.

Results.—These are assembled in the following table, in the headline of which "Mol.-fraction HX" denotes the mean molecular fraction of hydrogen halide in its mixture with the solvent (if any) during the progress of the reaction, and "Primary %" represents the percentage of primary halide in the alkyl halides formed by addition. The temperature throughout was 18° ± 2°.

Reagents.	Solvent.	Mol.-fraction HX.	Primary %.
Propylene and hydriodic acid	—	1·00	22·1
	Propane	0·64	22·7
	,,	0·15	24·8
	Nitrobenzene	0·61	16·5
	,,	0·23	11·6
	,,	0·13	10·5
	Acetic acid	0·48	10·5
	,,	0·17	6·5
	,,	0·10	6·0
	Water	0·55	21·9
	,,	0·24	20·4
	,,	0·19	14·6
	,,	0·16	3·4
	,,	0·12	2·8
n-Δ^{α}-Amylene and hydrobromic acid	—	1·00	0·0
	Water	0·34	0·0
	,,	0·30	0·0
	,,	0·23	0·0
n-Δ^{α}-Amylene and hydriodic acid	—	1·00	1·7
	Water	0·24	0·0
	,,	0·16	0·0

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