# 308. *The System Allyl Alcohol–Iodine–Di-iodopropyl Alcohol.*

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The addition of halogens to organic compounds containing a double link has been studied in considerable detail (for references, see Williams and James, J., 1928, 343). Specially interesting is that of bromine to α-phenylcinnamonitrile (Bauer and Moser, *Ber.*, 1907, **40**, 918) in carbon tetrachloride, a definite equilibrium dependent on the concentration being attained, as would be expected by analogy with a gas reaction of the second type. A corresponding reaction is that between allyl alcohol and iodine,

$$CH_2\colon CH\cdot CH_2\cdot OH + I_2 \rightleftarrows CH_2I\cdot CHI\cdot CH_2\cdot OH,$$

which in $M/40$-carbon tetrachloride solution gives an equilibrium of 70% of the addition product at 25°. This reaction has been investigated at various dilutions in carbon tetrachloride, in other solutions, and at different temperatures, and the velocities have been determined in both directions in the dark and also in light.

The allyl alcohol was repeatedly distilled with carbon tetrachloride to remove the last trace of water and finally boiled constantly at 97·0°/760 mm. The different solvents were specially purified and tested in particular for unsaturation by halogens. For the reactions in light there was an arbitrarily constant illumination from an electric lamp filtered through yellow glass. The reaction vessels were uniform and kept at a fixed distance from the source of illumination. The whole was contained in an insulated box where the temperature was constant at 24°. For the reaction in the dark, blackened bottles were used in a thermostat at 25°. The measurements at 50° were carried out in sealed glass tubes enclosed in light-proof containers filled with the liquid of the thermostat in which they were placed.

The solutions of iodine and allyl alcohol were prepared by weighing the material to 1 mg. of the required amount and made up to the required volume in the cold. The original concentration of the reacting components was made 0·025 molar. On attaining the thermostat temperature equal quantities of the solutions were pipetted into the reaction vessel and immediately after mixing a sample was withdrawn and titrated with 0·01$N$-thiosulphate. This procedure was then repeated at appropriate intervals.

For the investigation of the reverse action, di-iodopropyl alcohol was prepared by the direct union of finely ground iodine and allyl alcohol (Hübner and Lellmann, *Ber.*, 1881, **14**, 207), washed with dilute alkali solution and water, and rapidly dried on filter-paper, a portion made up in the required solvent, and the course of the reaction followed by titration of portions at intervals.

Williams and James (*loc. cit.*) found that the addition of halogens to unsaturated carbon compounds in solution proceeded by a mechanism which varied with the type of unsaturated compound involved. In some reactions there was catalysis by halogen ions and in others there was uncatalysed bimolecular addition. Polissar (*J. Amer. Chem. Soc.*, 1930, **52**, 956) found that in solution the action of iodine on ethylene was catalysed by iodine atoms at higher temperatures but not at lower temperatures. The present work shows that the action of iodine on allyl alcohol is reversible. If the simplest bimolecular and unimolecular mechanisms of the direct and the reverse reaction are assumed, the rate of formation of the addition compound is expressed as $dx/dt = k_1(a - x)^2 - k_2x$, where $k_1$ and $k_2$ are the velocity coefficients of the respective reactions, $a$ = initial concentration of the reacting compounds or compound, and $x$ = final concentration of the addition compound after time $t$. With the ratio $k_1/k_2$ replaced by $K$, the equilibrium constant for the system, and the substitution of $k_2$, this expression becomes

$$k_1 = dx/dt\,.\,1/\{(a - x)^2 - x/K\}.$$

An integration of this resulted in a cumbersome and unworkable expression. Therefore the term $x/K$, which is comparatively small in the earlier stages of the direct reaction, was omitted and $k_1$ was calculated from the integration of the simplified expression, which is that of a reaction of the second order. The constancy of the results in the period after slight initial disturbances and before the reverse reaction became appreciable is an indication that the iodine is not acting catalytically. Moreover, calculation of the velocity coefficients for reactions of the order $n$, where $n = 3/2, 2, 5/2$, and 3, gave the most constant results for $n = 2$. A further confirmation was obtained by employing the van 't Hoff method for experiments at different concentrations in carbon tetrachloride. At a concentration of $M/40$ the time for a 20% change was 55 hours, and at $M/80$ the time was 117 hours, giving a value of $n = 2·1$.

In the same way the reverse reaction, the decomposition of di-iodopropyl alcohol, is apparently unimolecular, although the falling off in the rate with time due to the opposing reaction is not so great as might be expected. In this change, then, it may be assumed that the iodine has a slight disturbing effect, which naturally becomes more marked as the decomposition proceeds and the iodine increases in amount.

There follow tables showing the values of $k_1$ ($n = 2$), the direct reaction, and $k_2$ ($n = 1$), the reverse reaction; the concentrations are $M/40$ and the temperature 25°.

TABLE I.

*Reaction in Carbon Tetrachloride Solution.*

| Time, hrs. | $k_1$ (dark). | Time, hrs. | $k_1$ (light). | Time, hrs. | $k_2$ (dark). | Time, hrs. | $k_2$ (light). |
|---|---|---|---|---|---|---|---|
| 44 | 0·093 | 8 | 2·86 | 41 | 0·000434 | 8 | 0·00943 |
| 55 | 0·092 | 18 | 2·17 | 119 | 0·000444 | 19 | 0·00979 |
| 116 | 0·108 | 27 | 1·75 | 453 | 0·000451 | 27 | 0·00867 |
| 147 | 0·102 | 63 | 0·88 | 498 | 0·000425 | 42 | 0·00590 |
| 400 | 0·096 | 111 | 0·58 | 598 | 0·000383 | 111 | 0·00266 |
| 481 | 0·087 | 498 | 0·13 | 832 | 0·000369 | 488 | 0·00061 |
| 549 | 0·084 | | | 1002 | 0·000315 | | |
| 652 | 0·072 | | | | | | |
| 820 | 0·060 | | | | | | |
| 1008 | 0·050 | | | | | | |
| 1510 | 0·027 | | | | | | |

The experimental values showing the formation of the di-iodopropyl alcohol are plotted in Fig. 1.

It is apparent that the equilibrium in the dark shows 72% formation of the addition compound, and in the light 75%, that is, almost the same within the limits of experimental error. In Table II are given the velocities in toluene solution and Fig. 2 shows the experimental values.

TABLE II.

*Reaction in Toluene Solution.*

| Time, hrs. | $k_1$ (dark). | Time, hrs. | $k_1$ (light). | Time, hrs. | $k_2$ (dark). | Time, hrs. | $k_2$ (light). |
|---|---|---|---|---|---|---|---|
| 23 | 0·0147 | 16 | 0·323 | 119 | 0·000238 | 23 | 0·00443 |
| 75 | 0·0199 | 34 | 0·412 | 168 | 0·000242 | 51 | 0·00437 |
| 122 | 0·0159 | 48 | 0·384 | 454 | 0·000228 | 68 | 0·00475 |
| 242 | 0·0244 | 71 | 0·322 | 498 | 0·000239 | 92 | 0·00440 |
| 330 | 0·0208 | 116 | 0·255 | 647 | 0·000244 | 142 | 0·00346 |
| 505 | 0·0233 | 192 | 0·165 | 1003 | 0·000260 | 237 | 0·00203 |
| 1176 | 0·0152 | 261 | 0·125 | | | | |

Here again the equilibrium seems to be independent of the illumination, there being formed in the light 62% of the addition compound, which is the amount calculated for the dark reaction by extrapolation.

The reaction has been studied also in benzene solution. The velocities in each direction are slower than in the other solvents, and the equilibrium value in the dark had to be calculated by extrapolation. The direct reaction in the dark shows a noticeable regularity, whereas the reverse reaction is accelerated slightly as it proceeds, possibly owing to the catalytic effect of the liberated iodine. In the light, however, the values of the velocity constant of the reverse reaction, after the initial disturbance, decrease regularly in accordance with expectation. This comparatively rapid falling off in $k_2$ (light) was noticed also for carbon tetrachloride, but not for toluene solution.

FIG. 1.

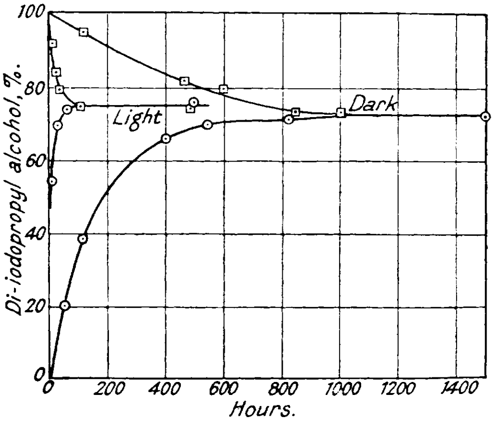

FIG. 2.

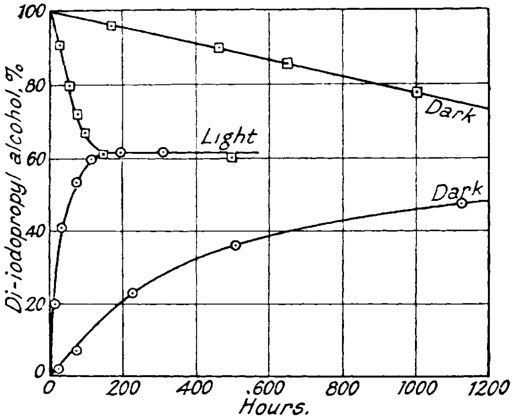

TABLE III.

*Reaction in Benzene Solution.*

| Time, hrs. | $k_1$ (dark). | Time, hrs. | $k_1$ (light). | Time, hrs. | $k_2$ (dark). | Time, hrs. | $k_2$ (light). |
|---|---|---|---|---|---|---|---|
| 113 | 0·0098 | 2 | 0·65 | 170 | 0·000084 | 5 | 0·0081 |
| 335 | 0·0094 | 5 | 0·62 | 329 | 0·000073 | 22 | 0·0118 |
| 540 | 0·0099 | 11 | 0·69 | 496 | 0·000090 | 39 | 0·0109 |
| 677 | 0·0098 | 18 | 0·69 | 647 | 0·000082 | 66 | 0·0071 |
| 827 | 0·0092 | 28 | 0·60 | 834 | 0·000094 | 92 | 0·0055 |
| 996 | 0·0097 | 44 | 0·46 | 1007 | 0·000114 | 142 | 0·0039 |
| 1164 | 0·0086 | 98 | 0·27 | | | 226 | 0·0027 |
| 1332 | 0·0089 | 171 | 0·15 | | | | |

Similar results were obtained with hexane as a solvent. The average values of the reaction velocities and the equilibrium data for all four solvents are in Table IV.

TABLE IV.

| Solvent ($V = 20$). | $k_1$ (dark). | $k_2$ (dark). | Equilibrium, %. | $k_1$ (light). | $k_2$ (light). | Equilibrium, %. |
|---|---|---|---|---|---|---|
| $CCl_4$ .................. | 0·098 | 0·00043 | 72 | 2·51 | 0·0376 | 75 |
| $C_6H_6$ .............. | 0·0096 | 0·000085 | 66 | 0·65 | 0·0103 | 60 |
| $C_7H_8$ .............. | 0·0199 | 0·00024 | 62 | 0·37 | 0·0045 | 60 |
| $C_6H_{14}$ .............. | 2·14 | — | 74 | — | — | — |

It is seen that within the limits of experimental error the equilibrium is not affected by light, and does not vary greatly in the different solvents. In particular the behaviour in hexane is outstanding, with a velocity considerably greater than for the other solvents. This difference has little effect on the equilibrium, and is difficult to explain, as all the four solvents are non-polar compounds with low dielectric constants.

The effect of change of volume on the equilibrium is shown in the following figures from reactions in carbon tetrachloride in the dark at 25° between iodine and allyl alcohol. The value of $K$, the equilibrium constant, is calculated from the expression $K = V\varepsilon/(a - \varepsilon)^2$, where $\varepsilon$ is the equilibrium concentration of the addition compound.

TABLE V.

| | | | | |
|---|---|---|---|---|
| Concentration | $M/40$ | $M/80$ | $M/160$ | $M/320$ |
| Equilibrium, % | 72 | 65 | 56 | 42 |
| $K$ | 183 | 215 | 231 | 193 |

The value of $K$ can be calculated also from the relationship $K = k_1/k_2$, and the average result obtained from experiments at concentrations $M/40$ and $M/80$ was 205, which is in satisfactory agreement with the values in Table V.

The values of the equilibrium constant have also been calculated by both methods for the other solvents, and the results are in Table VI. The carbon tetrachloride results are the average of different dilutions.

TABLE VI.

| | $K$ (dark). | | $K$ (light). | |
|---|---|---|---|---|
| Solvent. | $k_1/k_2$. | $V\varepsilon/(a - \varepsilon)^2$. | $k_1/k_2$. | $V\varepsilon/(a - \varepsilon)^2$. |
| $CCl_4$ | 205 | 205 | 262 | 216 |
| $C_7H_8$ | 83 | 88 | 82 | 77 |
| $C_6H_6$ | 114 | 75 | 66 | 75 |

When the nature of the experiments is taken into account, and more especially the difficulty of computing the true values of $k_1$ and $k_2$, it is seen that the conclusion with regard to the influence of light on the equilibrium is confirmed.

The reaction has also been examined at 50°, and Table VII gives the results for carbon tetrachloride solution at $M/40$ in the dark.

TABLE VII.

| | | | | | |
|---|---|---|---|---|---|
| Time, hrs. | 8 | 22 | 42 | 80 | 145 |
| $k_1$ | 0·296 | 0·183 | 0·114 | 0·104 | 0·062 |
| Time, hrs. | 160 | 329 | 742 | 1007 | |
| $k_2$ | 0·00044 | 0·00079 | 0·00073 | 0·00064 | |

It is seen that the rate of the direct reaction falls even before the effect of the opposed reaction should be appreciable. The mechanism seems therefore to be somewhat different from that at the lower temperature. The reverse reaction, on the other hand, shows an initial irregularity. The same equilibrium is reached in both reactions; it amounts to 49% iodo-alcohol formation, in comparison with 72% at 25°. The value of the equilibrium constant at 50° is 40, and if this result is used in the van 't Hoff isochore for the two temperatures 25° and 50°, it can be calculated that the heat of the reaction $CH_2{:}CH{\cdot}CH_2{\cdot}OH + I_2 \longrightarrow CH_2I{\cdot}CHI{\cdot}CH_2{\cdot}OH$ has a value of + 12·3 Calories.

## SUMMARY.

(1) The dissociation of di-iodopropyl alcohol into allyl alcohol and iodine, and the reverse reaction, have been studied in carbon tetrachloride solution.

(2) The system corresponds with a gas reaction of the second type : the dissociation at 25°, which is 28% ($V = 20$), changes to 58% ($V = 160$) in accordance with the law of mass action.

(3) The two reactions are greatly accelerated by light, but the equilibrium remains unaltered.

(4) Solvents influence the rates of the opposing reactions, but have little effect on the final equilibrium.

(5) A change of temperature from 25° to 50° increases the amount of dissociation from 28% to 51% in carbon tetrachloride solution ($V = 20$).

(6) The dissociation is unimolecular, and the reverse reaction bimolecular, and the reactions appear only slightly sensitive to catalytic disturbances, either in the light or in the dark.

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