

Hypoiodite Reaction: Kinetic Study of the Reaction of 1,1-Diphenylethylene with Mercury(II) Oxide-Iodine

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Rate studies and product analyses for the reactions of 1,1-diphenylethylene, 1,1-diphenylethylene oxide, and 2-iodo-1,1-diphenylethanol with mercury(II) oxide-iodine have shown that the reaction with the olefin is a combination of parallel steps which produce 2,2-diphenylvinyl iodide and 2-iodo-1,1-diphenylethyl hypoiodite and a consecutive reaction of 2-iodo-1,1-diphenylethyl hypoiodite, which produces phenylacetophenone. The consecutive reaction, however, only takes place after the reaction solution is depleted of olefin, which, it is suggested, stabilizes the iodo-hypoiodite.

THE reaction of olefins with mercury(II) oxide-iodine has been shown to proceed in accord with a regio-specific ionic addition mechanism.^{1a} Evidence has been presented that the reactive species from the reagent is 'iodine oxide,'^{1b} and the stability and reactivity of the reagent have been investigated.^{1c} This paper describes the relative rates of formation and stabilities of the products derived from 1,1-diphenylethylene.

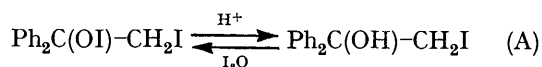
1,1-Diphenylethylene has been shown to produce phenylacetophenone and 2,2-diphenylvinyl iodide (3).^{1a} A trace of benzophenone has subsequently been detected also. The kinetic experiments were carried out on 1,1-diphenylethylene in dry carbon tetrachloride with a six-

¹ C. P. Forbes, A. Goosen, and H. A. H. Laue, (a) *J. S. African Chem. Inst.*, 1972, **25**, 144; (b) preceding paper; (c) *J. S. African Chem. Inst.*, 1972, **25**, 328.

fold excess of mercury(II) oxide-iodine. Samples were withdrawn at intervals, washed with aqueous 10% sodium thiosulphate, treated with standard benzophenone solution (internal standard), and subjected to g.l.c. analysis. The reaction was carried out at 21.6° over a period of 70 min.

The results showed the smooth disappearance of starting material and appearance of the vinyl iodide (3) as well as the appearance and disappearance of 2-iodo-1,1-diphenylethanol and 1,1-diphenylethylene oxide, which both seemed to be intermediates. The rate of formation of phenylacetophenone was initially negligible and increased markedly only after the two apparent intermediates began to disappear (Figure 1).

Figure 1 shows that the formation of the ketone is dependent on the disappearance of epoxide and iodohydrin. However, 1,1-diphenylethylene oxide is cleaved under these conditions to produce benzophenone.^{1b} Since only a small amount of benzophenone was produced in the overall reaction the presence of substantial amounts of epoxide required further investigation. Accordingly, 1,1-diphenylethylene was treated with mercury(II) oxide-iodine and samples were withdrawn as before. Each sample was divided in two and one portion was quenched with aqueous sodium thiosulphate. The n.m.r. spectrum of the unquenched portion was run directly and the quenched portion analysed, as before, by g.l.c. The quenched samples contained the epoxide and a small amount of 2-iodo-1,1-diphenylethanol but the n.m.r. spectrum of the unquenched samples showed resonances due to 2-iodo-1,1-diphenylethanol without any detectable epoxide. We concluded that the reaction solution does not contain any appreciable amount of the epoxide, as was evident from the absence of epoxide signals in the n.m.r. spectrum of the unquenched samples, and the epoxide must therefore be formed during work-up, from the iodo-hypoiodite or iodohydrin. The epoxide was shown not to be derived from the iodohydrin by separate experiments in which the iodohydrin was synthesized, which involved the same work-up procedures without resulting in any epoxide formation. This implies that, apart from small amounts of iodohydrin, only the iodo-hypoiodite is present in the reaction solution, and work-up produces the epoxide. Surprisingly, only the iodohydrin is apparent in the n.m.r. spectra of the unquenched samples. According to the foregoing hypothesis, the presence of the iodo-hypoiodite would be expected. This can be explained on the basis of an equilibrium (A) in the reaction solution between the iodo-hypoiodite and the iodohydrin, the hydrogen ions involved being produced during the formation of the



vinyl iodide. The temperature increase as well as the exposure of the sample which occurs during the running of the n.m.r. spectrum would cause decomposition of

the iodine oxide resulting in a shift of this equilibrium to the right.

By utilizing 1,2-diphenylethane-1,2-diol, which has been shown^{1c} to be cleaved rapidly to benzaldehyde upon treatment with mercury(II) oxide-iodine, as a standard to monitor the reactivity of the positive iodinating reagent, an n.m.r. study of the above exchange reaction of hydroxy-protons with positive iodine was undertaken, with cyclohexanol as substrate. Whereas the reaction with the diol proceeded smoothly to completion the reaction of cyclohexanol, monitored by comparing the intensity of the $\text{CH}\cdot\text{OH}$ n.m.r. signal with the total intensity of the high-field resonances including the OH signal, showed that the equilibrium corresponding to (A) lies almost completely to the right.

A separate experiment on 2-iodo-1,1-diphenylethanol under the same conditions as used for the olefin showed that the iodohydrin was entirely converted into phenylacetophenone in 17 min. However, Figure 1 shows that

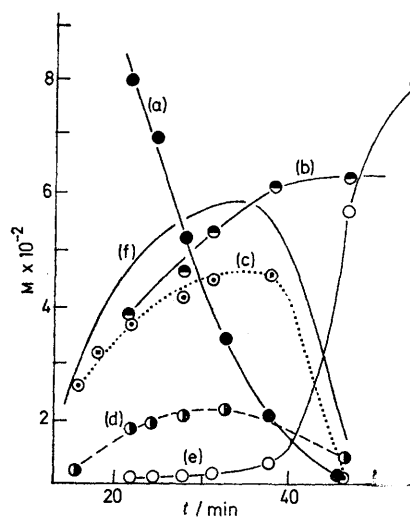
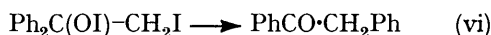
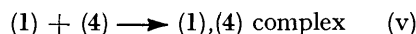
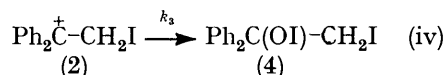
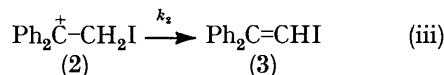
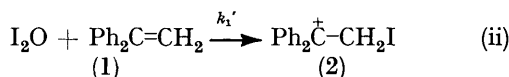
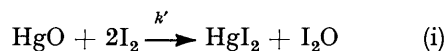


FIGURE 1 Reaction of 1,1-diphenylethylene with mercury(II) oxide-iodine (molarities of reactant and products vs. time); (a) olefin, (b) vinyl iodide, (c) epoxide, (d) iodohydrin, (e) ketone, (f) epoxide + iodohydrin

the ketone is formed only after about 42 min. Hence the iodo-hypoiodite must be stabilized. The stabilizing agent cannot be iodine oxide, since this was present in both experiments, nor can it be the vinyl iodide since the concentration of the latter is at a maximum when phenylacetophenone formation is occurring (Figure 1). The only feasible explanation seems to be that the iodo-hypoiodite is stabilized by the olefin. This fact was verified by repeating the experiment with the iodo-hydrin in the presence of an equimolar amount of the olefin. Ketone formation was almost completely inhibited for at least double the time for total ketone formation in the absence of the olefin. The nature of this stabilization was further investigated. The curves for iodohydrin and epoxide (Figure 1) were added and the resultant curve (which represents the total amount of iodo-hypoiodite in solution) had a maximum at $t = 33$ min. At this time the molarity of the olefin is

ca. one half the molarity of the iodo-hypoiodite. This suggests that one olefin molecule is stabilizing two iodo-hypoiodite molecules. When the olefin concentration falls below this value the iodo-hypoiodite is no longer effectively stabilized and ketone formation begins, rapidly reaching a maximum a short time after the olefin concentration has fallen to zero.

A kinetic scheme for the initial period of the reaction was derived on the basis of the reactions (i)–(vi).



The expressions (vii) and (viii) for the variation of the concentrations of 1,1-diphenylethylene (1) and 2,2-

$$\ln(A_0/A) = k_1 t \quad (\text{vii})$$

$$-\ln(1 - C/H) = k_1 t \quad (\text{viii})$$

diphenylvinyl iodide (3), were obtained by using the steady state approximation $d[(2)]/dt = 0$, where A_0 and A are the initial concentration and the concentration at time t of 1,1-diphenylethylene, $k_1 = [\text{I}_2\text{O}]k_1'$, $C =$ concentration of 2,2-diphenylvinyl iodide at time t , and $H = [k_2/(k_2 + k_3)]A_0$. A plot of $\ln(A_0/A)$ as a function of time gave a straight line (Figure 2) in agreement with

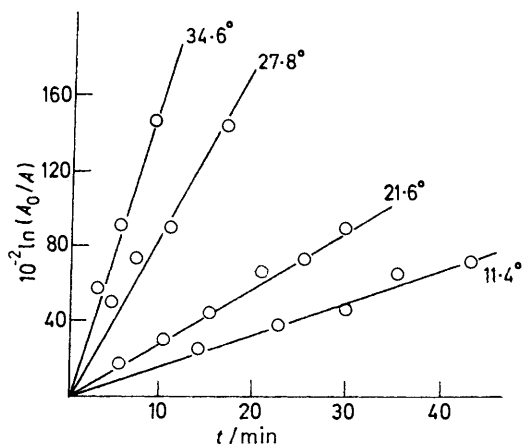


FIGURE 2 $\ln(A_0/A)$ vs. t (for olefin disappearance)

first-order kinetics. This can only occur if the concentration of iodine oxide is invariant (as required by the derivation). A series of four reactions was then carried out at temperatures in the range 11.4–34.6°. The rate constants (k_1) are given in Table I. An Arrhenius plot gave an activation energy of 20 kcal mol⁻¹.

Despite the first-order plot, it is realized that a meaningful value cannot be attached to the determined rate constants or activation energy if the concentration

TABLE I

Reaction of 1,1-diphenylethylene with mercury(II) oxide–iodine

Temp. (°C)	11.4	21.6	27.8	34.6
$10^5 k_1/s^{-1}$	29.0	49.2	153.1	258.0

of the olefin is reduced by complexation with the iodo-hypoiodite [reaction (v)]. In support of the participation of reaction (v), plots of $\ln(1 - C/H)$ as a function of time were not linear (Figure 3).

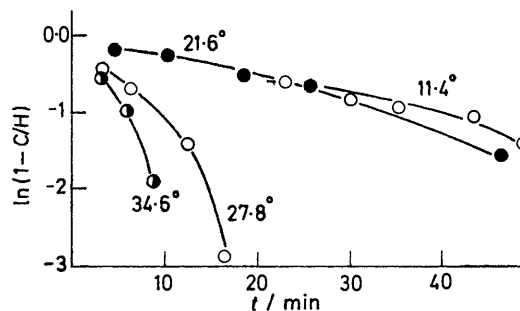


FIGURE 3 $\ln(1 - C/H)$ vs. t (for vinyl iodide appearance)

The reaction sequence is thus a combination of parallel reactions (iii) and (v) and a consecutive reaction (vi) which is inhibited by the complex-forming reaction (v).

EXPERIMENTAL

Kinetics of the Reaction of Mercury(II) Oxide–Iodine with 1,1-Diphenylethylene.—General procedure. Iodine (47.6 g, 112.5 mmol) in dry carbon tetrachloride (60 ml), in a flask coated with aluminium foil immersed in a thermostatted water-bath and fitted with a stirrer, was treated with red mercury(II) oxide (40.7 g, 112.5 mmol). The solution was stirred for 7 min and 1,1-diphenylethylene (3.39 g, 18 mmol) was added. Samples (2 ml) were withdrawn, added to aqueous 10% sodium thiosulphate (2 ml) and shaken. A standard benzophenone solution was added (0.29M; 1 ml) and the mixture was shaken and filtered through cotton wool under vacuum.

G.l.c. analyses (column 0.3 × 336 cm glass spiral packed with 1% silicone Dow 11 on Chromport XXX, 60–70 mesh; temp. 190°; retention times 2-iodo-1,1-diphenylethanol 440 s, benzophenone 184 s, 1,1-diphenylethylene oxide 210 s, phenylacetophenone 236 s, 1,1-diphenylvinyl iodide 374 s) were performed by comparisons with standard solutions of the compounds which had been subjected to the same work-up procedure. Calibration curves were plotted of the benzophenone: compound peak ratio as a function of the molarity of the relevant compound. From curves, the molarity of the required compound could be determined. The results are summarized in the Figures.

In the experiments carried out on 1,1-diphenylethylene oxide, 2-iodo-1,1-diphenylethanol, and an equimolar mixture of the olefin and the iodoalcohol, identical conditions were employed.

2-Iodo-1,1-diphenylethanol.—1,1-Diphenylethylene (40 mmol) in ether (150 ml) was treated with mercury(II) oxide–iodine (40 mmol), and water (5 ml) was added. The

mixture was shaken for 22 h, filtered, washed with an excess of aqueous 10% sodium thiosulphate and water, dried (Na_2SO_4), and concentrated to an oil which was separated by chromatography on silica gel to give 2-iodo-1,1-diphenylethanol, m.p. 58–59° (from petroleum, b.p. 80–100°), δ (CDCl_3) 2.85 (1H, s), 4.00 (2H, s), and 7.35 (10H, m). Reduction of the product with an excess of lithium aluminium hydride in ether gave 1,1-diphenylethanol, identical with an authentic specimen.

Exchange of Hydroxy-protons with Positive Iodine.—Two flasks, coated with aluminium foil were each charged with deuteriochloroform (10 ml), iodine (3.79 g, 15 mmol), and substrate (0.5 mmol). Red mercury(II) oxide (0.808 g, 3.75 mmol) was added, the mixtures were shaken and samples were withdrawn at intervals and analysed by n.m.r. spectroscopy.

The decrease in 1,2-diphenylethane-1,2-diol concentration was monitored by comparing the intensity of the $\text{CH}\cdot\text{OH}$

signals (δ 6.8) with that of the aromatic proton signals (δ 2–3) (Table 2).

The exchange of the hydroxy proton of cyclohexanol was monitored by comparing the intensity of the $\text{CH}\cdot\text{OH}$ signal (δ 3–4) with that of the high-field signals (δ 0.9–2.3), which included the OH resonance.

TABLE 2

Reaction of 1,2-diphenylethane-1,2-diol with mercury(II) oxide-iodine

t/h	0	0.083	0.25	0.5	0.83	14.0
% Diol	100	80	64	51	44	0

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