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PHOTOCHEMICAL IODINATION OF TRIETHYLBORANE

M. ABUFHELE, C. ANDERSEN, E. A. LISSI and E. SANHUEZA
Departamento de Química, Universidad Técnica del Estado, Santiago (Chile)
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SUMMARY

The photochemical iodination of triethylborane in cyclohexane solutions takes place through a simple free-radical mechanism from 50–90°. The mechanism becomes complex at lower temperatures and high iodine concentration.

The rate expression for the chain reaction is given by

$$-\mathrm{d}[\mathrm{I_2}]/\mathrm{d}t = k \times I_a^{\frac{1}{2}} + [\mathrm{Et_3B}]$$

with

$$\log_{10} k = 3.4 - 10{,}200/4.6\ T$$

(mol l^{-1} is employed as the unit of concentration)

The rate determining step is the attack of an iodine atom on a triethylborane molecule. The rate constant for this step was

$$\log_{10} k_2 = 9.4 - 11{,}700/4.6\ T$$

in reasonable agreement with the value obtained at higher temperatures from the thermal reaction.

INTRODUCTION

In a previous paper[1] we showed that the thermal reaction between triethylborane (TEB) and iodine can be interpreted in terms of a free radical mechanism such as

$$\mathrm{I_2} \rightleftharpoons 2\,\mathrm{I^{\bullet}} \tag{1}$$

$$\mathrm{I^{\bullet}} + \mathrm{TEB} \rightleftharpoons \mathrm{IBEt_2} + \mathrm{Et^{\bullet}} \tag{2}$$

$$\mathrm{Et^{\bullet}} + \mathrm{I_2} \rightarrow \mathrm{EtI} + \mathrm{I^{\bullet}} \tag{3}$$

On the other hand, preliminary results[2] obtained for the photochemical reaction at 30° were compatible with a rate expression such as

$$-\mathrm{d}[\mathrm{I_2}]/\mathrm{d}t = k \times I^{\frac{1}{2}} \times [\mathrm{TEB}][\mathrm{I_2}]^{\frac{1}{2}} \tag{4}$$

and showed an increase in the reaction rate with conversion. These results were tentatively interpreted by assuming the participation of an iodine atom, an iodine molecule and a TEB molecule in the rate determining step. To clarify the difference between both mechanisms, the photochemical reaction was reinvestigated under a wider range of experimental conditions.

EXPERIMENTAL

The experimental technique was similar to that previously described[1]. Light employed was either obtained from a tungsten filament lamp and filtered through a soda glass, or green light with its maximum intensity at about 5100 Å. Quantum yields were obtained by employing allyl iodide as an actinometer.

The light intensity (I_i) was changed by varying the distance between the light source and the reaction cell. The spectral distribution of the light employed was thus independent of the light intensity. Under these conditions, at a given iodine concentration, the absorbed light intensity (I_a) will be proportional to I_i. Furthermore, as the light path is short, at low iodine concentration and constant I_i the absorbed intensity will be proportional to the iodine concentration.

RESULTS AND DISCUSSION

Results obtained at 50° are shown in Fig. 1. It can be seen from this figure that the shape of these plots is considerably different from those obtained previously at lower temperatures[2]. At 70 and 90° the behaviour was similar to that observed at 50°.

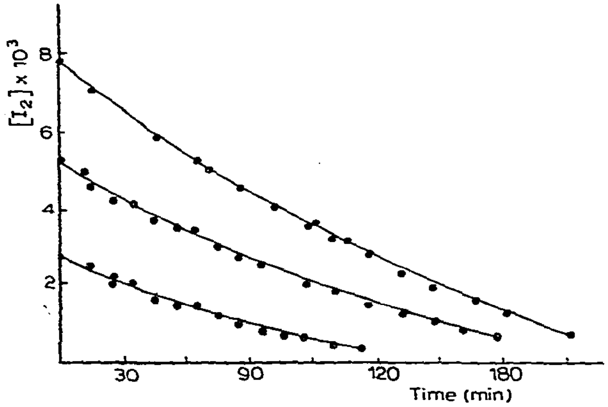

Fig. 1. Iodine consumption as a function of time. Temperature: 50°. TEB concentration: 0.12 mol l^{-1}. Wavelength longer than 3200 Å.

At 50° the relationship between initial slope and iodine concentration indicated a 0.5 order in iodine. To test this, the data obtained were plotted according to the integrated equation[1], eqn. (5),

$$[I_2]_0^{\frac{1}{2}} - [I_2]^{\frac{1}{2}} = k/2\,[\text{TEB}]\,t \tag{5}$$

where [TEB] was considered as constant.

A plot of $\Delta[I_2]^{\frac{1}{2}}$ against time is shown in Fig. 2 for three runs carried out at the same initial TEB concentration but different initial iodine concentrations. The

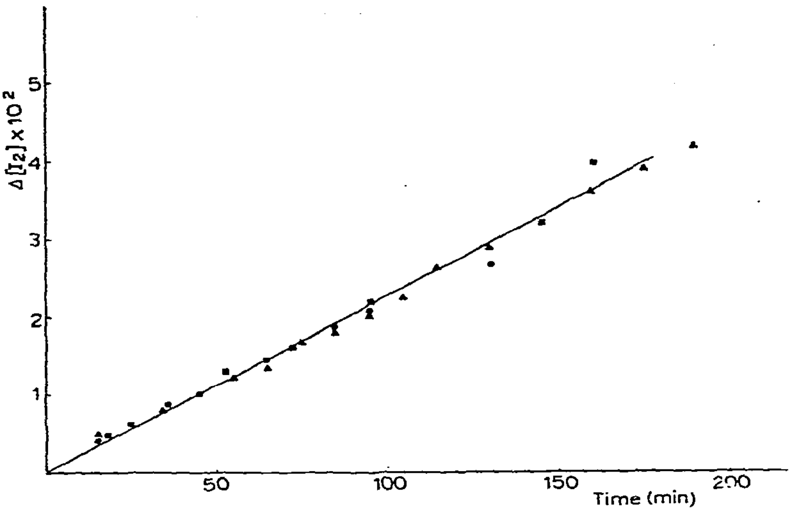

Fig. 2. Plot of $[I_2]_0^{\frac{1}{2}}-[I_2]_t^{\frac{1}{2}}$ against time. Temperature: 50°. ▲, ■, ●, TEB concentration: 0.12 mol l^{-1}; ● $[I_2]_0=2.6\times10^{-3}$ mol l^{-1}; ▲ $[I_2]_0=5.1\times10^{-3}$ mol l^{-1}; ■ $[I_2]_0=7.7\times10^{-3}$ mol l^{-1}.

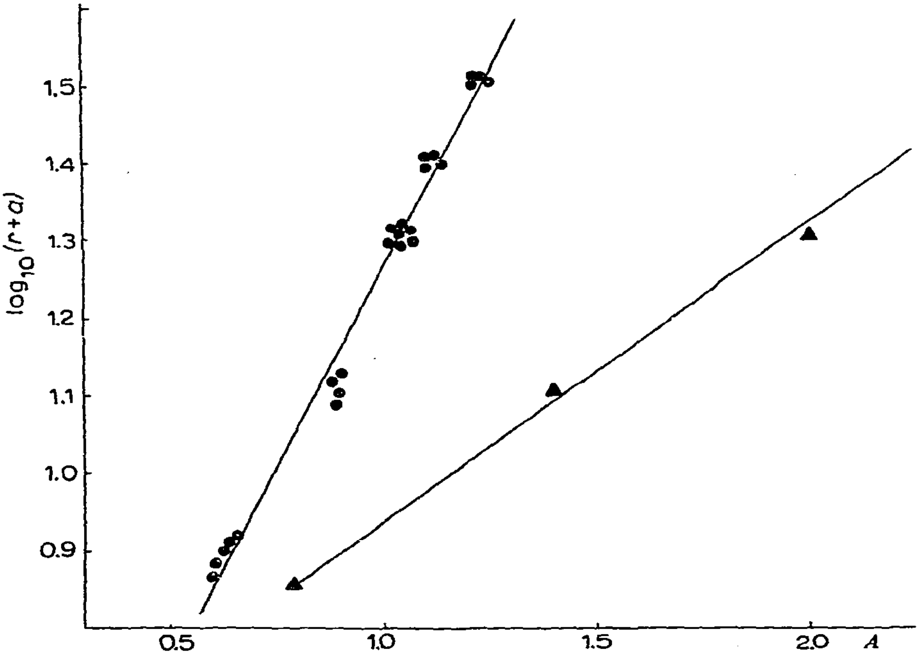

Fig. 3. Order in TEB concentration and light intensity. ● $r=v/[I_2]^{\frac{1}{2}}$; $a=0$; $A=\log_{10}[\text{TEB}]+2$; ▲ $r=v/[I_2]^{\frac{1}{2}}[\text{TEB}]$; $a=1$; $A=\log_{10} I_i$; $v=-d[I_2]/dt$; I_i is given in arbitrary units.

linearity of this plot (up to nearly 80% conversion) as well as the fact that different initial iodine concentrations give undistinguishable results, shows that the order in iodine is 0.5. Furthermore, the same order is obtained regardless of changes in initial concentration or changes due to conversion. This fact shows that under the present conditions no autoacceleration is present[2].

The results obtained by changing the light intensity or the initial TEB concentration are shown in Fig. 3. From this Figure, it can be concluded that the order in light intensity is nearly 0.5 and that the order in TEB is 1.0. This then gives

$$-\mathrm{d}[\mathrm{I}_2]/\mathrm{d}t = k_6 \times (I_i)^{\frac{1}{2}} \times [\mathrm{I}_2]^{\frac{1}{2}} \times [\mathrm{TEB}] \tag{6}$$

This equation can be rearranged to

$$-\mathrm{d}[\mathrm{I}_2]/\mathrm{d}t = k_7 \times (I_a)^{\frac{1}{2}} \times [\mathrm{TEB}] \tag{7}$$

Equation (7) holds up to at least 80% iodine conversion and 60% TEB conversion.

A mechanism compatible with this rate expression involves the following reactions

$$\mathrm{I}_2 + h\nu \longrightarrow 2\,\mathrm{I}^{\bullet} \tag{8}$$

$$\mathrm{I}^{\bullet} + \mathrm{I}^{\bullet} \longrightarrow \mathrm{I}_2 \tag{9}$$

together with reactions (2) and (3). If we consider that:

$$\text{Rate of reaction (8)} = \phi_{\mathrm{I}^{\bullet}} \times I_a \tag{10}$$

where

$\phi_{\mathrm{I}^{\bullet}}$ = quantum yield of free $\mathrm{I}^{\bullet}$ production ,

we obtain

$$-\mathrm{d}[\mathrm{I}_2]/\mathrm{d}t = (\phi_{\mathrm{I}^{\bullet}} \times I_a)^{\frac{1}{2}} \times k_2[\mathrm{TEB}]/k_9^{\frac{1}{2}} \tag{11}$$

and

$$\phi_{\mathrm{EtI}} = \mathrm{Rate}/(\phi_{\mathrm{I}^{\bullet}} \times I_a) = k_2[\mathrm{TEB}]/(\phi_{\mathrm{I}^{\bullet}} \times I_a k_9)^{\frac{1}{2}} \tag{12}$$

Values of $(\phi_{\mathrm{I}^{\bullet}} \times I_a)$ were obtained from measurements of the rate of iodine formation during the photolysis of mixtures of iodine, allyl iodide and oxygen[3,4].

The quantum yields obtained by applying equation (12) show that under our experimental conditions the reaction involves the occurrence of very short chains. For example, when

$$\phi_{\mathrm{I}^{\bullet}} \times I_a = 1.2 \times 10^{-7}\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$$

and

$$[\mathrm{TEB}] = 0.31\ \mathrm{mol\ l}^{-1}$$

the quantum yield obtained at 50° was approximately 0.4.

Results at 30°

Results obtained at 30° showed a behaviour similar to that reported previously[2]. On the other hand, when the kinetics were followed at lower iodine concentrations, the results were compatible with eqn. (7). The "S" shaped iodine consumption curve is thus only obtained at low temperatures and high iodine concentrations. These facts suggest a relationship between this type of behaviour and the formation of some complex involving an iodine molecule. A mechanism comprising reactions (2), (3), (8), (9) and

$$I_2+I^\bullet \rightleftharpoons I_3^\bullet \qquad (13)$$

$$I_3^\bullet+\text{TEB} \rightarrow \text{EtI}+\text{IBEt}_2+I^\bullet \qquad (14)$$

could explain most of the experimental results if it is assumed that reactions (13) and (14) would provide the main reaction pathway at low temperatures and high iodine concentrations.

Change of rate constant with temperature

Values of $k_2/k_9^{\frac{1}{2}}$ derived from eqn. (11) are shown in an Arrhenius type plot in Fig. 4. The value shown at 30° is that obtained at low $[I_2]$ and is in reasonable agreement with the values obtained at higher temperatures. From this plot it can be shown that

$$E_2-\tfrac{1}{2}\,E_9 = 10.2 \text{ kcal mol}^{-1}$$

and

$$A_2/A_9^{\frac{1}{2}} = 3.4 \text{ l}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ s}^{-\frac{1}{2}}$$

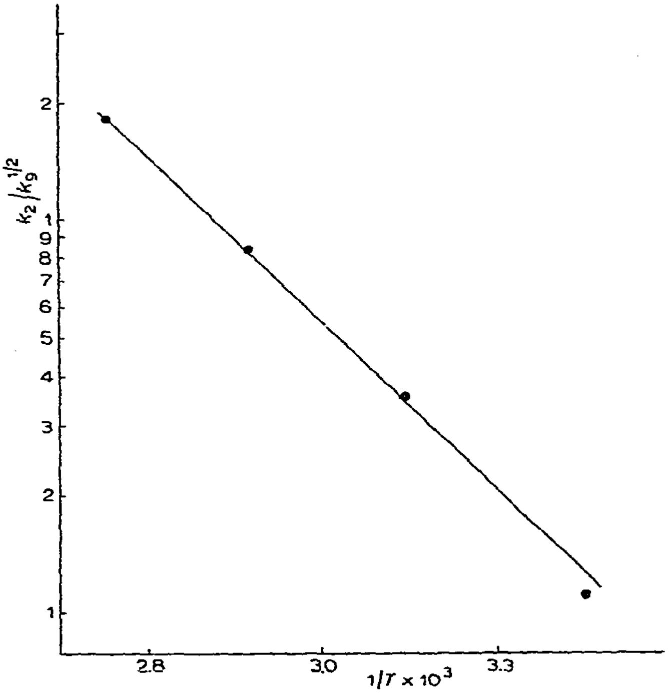

Fig. 4. Arrhenius plot for $k_2/k_9^{\frac{1}{2}}$.

The difference between the activation energies of the thermal and photochemical reactions is then nearly 17 kcal mol^{-1}. This value is in very good agreement with that found by Noyes and coworkers[5] in their studies of thermal and photochemical exchange between iodine and allyl iodide in hexane.

If we assume than the values of E_9 and A_9 are similar to those obtained employing carbon tetrachloride as solvent[6], we find that

$$\log_{10} k_2 = 9.4-11.7/2.3\ RT$$

in reasonable agreement with the value obtained in the thermal reaction[1]. The agreement between both sets of determinations is as good as can be expected from the kind of assumption involved in their determination.

The ΔH associated with reaction (2) can be evaluated from group contribution[7] if we assume that values derived from gas phase data can be applied to solution. The ΔH_f of $IBEt_2$ can be evaluated from equation (15)

$$\Delta H_f(IBEt_2) = 2(C\text{–}(C)(H)_3) + 2(C\text{–}(C)(H)_2(B) + (B\text{–}(C)_2(I)) \qquad (15)$$

and the values given by Benson[7] for the group contributions. This gives

$$\Delta H_f(IBEt_2) = 33.5 \text{ kcal mol}^{-1}$$

If this value is related to $\Delta H_f(I^{\cdot})$,$\Delta H_f(Et^{\cdot})$ and $\Delta H_f(Et_3B)$ (refs. 7 and 8), it can be shown that $\Delta H_2 = 3.2$ kcal mol^{-1}.

If we average the values of E_2 obtained in the thermal and photochemical reaction, this gives for reaction (16):

$$Et^{\cdot} + IBEt_2 \rightarrow Et_3B + I^{\cdot} \qquad (16)$$

an activation energy of nearly 7.7 kcal mol^{-1}. This value is of the same order of magnitude as that obtained for reaction (17):

$$CH_3^{\cdot} + Et_3B \rightarrow Et^{\cdot} + CH_3BEt_2 \qquad (17)$$

for which it was found[9] that $E_{17} = 5.2$ kcal mol^{-1}. The difference, if real, can be related to the higher reactivity of the methyl radical and to the steric strain introduced by the iodine atom.

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