REACTIONS OF IODINE ATOMS WITH *n*-BUTENES I. CIS-TRANS ISOMERIZATION OF BUTENE-2¹

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Received January 28, 1963

ABSTRACT

In the interaction of iodine atoms with butene-2 at 65° C no addition products are observed although cis-trans isomerization of the butene occurs readily. Iodine atoms have been generated by photolyzing iodine in three spectral regions. The limiting quantum yield of the isomerization reaction is about 0.1 at 4358 Å. The low quantum yield shows that chain reactions, similar to those observed in olefin photochlorinations and photobrominations, do not take place. A mechanism involving initial formation of π -complexes between iodine atoms and butene-2 is tentatively considered.

INTRODUCTION

A study of the relative rates of addition of various reagents to olefins in the gas phase has been in progress for the past several years (1). Such studies provide information on the nature of the process of addition to double bonds and whether in this process the attacking species behaves as an electrophilic, nucleophilic, or radical reagent. The variation of the rate constants for addition with structure of the olefins has shown that in their reactions with olefins, oxygen atoms (2) and ozone (3) behave as electrophilic reagents, while hydrogen atoms (4) have the character of radical (electroneutral) reagents. As an extension of this series a study of the addition of iodine atoms to olefins was begun and this paper reports the first results.

The photoiodination of the butenes, propylene, and ethylene in chloroform solution was studied by Forbes and Nelson (5) and quantum yields for disappearance of iodine were found to be of the order of 1. The addition product of iodine atoms with the butenes, diiodobutane, was found to be unstable at room temperature and the reaction was done at -70° C. Since the diiodobutane was not stable at temperatures required for the gas phase study (6), butene-2 was chosen for the reference olefin in the present work in the hope that the cis-trans isomerization would provide a measure of the rate of reaction of iodine atoms with the double bond.

EXPERIMENTAL

Materials

Reagent grade iodine was sublimed once and sealed off in a reservoir. Phillips Research Grade butene was used after two bulb-to-bulb distillations. *cis*-Butene was found to contain less than 0.1% *trans*-butene. Oxygen was prepared by heating potassium permanganate, and Red-band grade of nitrogen was obtained from Linde Air Company.

Apparatus

The experiments were done in a cylindrical Pyrex cell 10 cm long and 5 cm in diameter. A high-pressure mercury arc lamp, Mazda type ME/D, was used and a roughly parallel beam was obtained using a 250-cc flask as a spherical lens. A 935 phototube and microammeter, placed beyond the reaction vessel, were used to measure relative light intensities. The lamp, flask, reaction cell, and phototube were mounted on an optical bench and the reaction cell was enclosed in a thermostatted oven.

For experiments with light of wavelength greater than 5000 Å, Corning filter 3-69 was used and the

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Canadian Journal of Chemistry. Volume 41 (1963)

flask was filled with a dilute solution of copper sulphate. For some experiments a solution of NdCl₃ (7) was used to isolate the mercury line 5461 Å. For light of wavelength less than 5000 Å, a filter solution was made of 6.2 g of copper sulphate and 75 cc of concentrated ammonium hydroxide diluted to 1 liter (8). The flask provided a path length of about 8 cm for absorption. To isolate the mercury line 4358 Å, Corning filter 3-74 was used with this solution.

A few experiments were done using a low-pressure mercury resonance lamp and Corning filter 7-54. In

this case a quartz reaction vessel of similar dimensions replaced the Pyrex cell and the flask was not used. Iodine was admitted to the reaction vessel at its equilibrium vapor pressure from a constant-temperature reservoir through a heated stopcock. The pressure was calculated from the expression (9)

$$\log_{10} p_{\text{atm}} = -\frac{3512.8}{T} - 2.013 \log_{10} T + 13.3740.$$

The reaction vessel and iodine reservoir were separated from the main manifold by a large trap filled with glass beads and maintained at -78° C. This provided an effective means of keeping iodine from the main manifold and mercury from the reaction vessel.

Procedure

It was found necessary, in order to eliminate heterogeneous reaction, to avoid condensation of butene and iodine together. After allowing the iodine pressure to equilibrate for 10 minutes the reservoir was closed and butene admitted by momentarily connecting the reaction vessel to a bulb containing the appropriate quantity of gaseous butene. The pressure of butene always exceeded that of iodine so that no iodine escaped the cell. Nitrogen and oxygen were admitted in a similar manner from a much larger reservoir and in this case the pressure of nitrogen or oxygen was much greater than the combined pressures of iodine and butene.

Pressures of iodine ranged from 0.5 mm to 5 mm and of butene from 1 to 25 cm. Highest pressure of nitrogen used was 46 cm and of oxygen 20 cm. Most of the experiments were done at 65° C and at conversions of about 2%, where a back reaction could be neglected. Fine copper or nickel screens were used to reduce the incident light intensity.

Analysis

The hydrocarbon products were analyzed on a 50-ft gas chromatographic column of dimethylsulpholane on firebrick at 25° C.

Measurement of Light Intensity

Potassium ferrioxalate was used as an external actinometer (10) with light of wavelengths 4358 Å and 2537 Å. A cylindrical cell about 1 cm thick and of the same diameter as the reaction cell was placed first in front of and then behind the reaction vessel, and measurements were taken with and without iodine in the vessel.

RESULTS

The reaction of iodine atoms with *cis*-butene-2 caused isomerization to *trans*-butene-2 and at conversions of less than 3% no other products were observed. Experiments with long times of irradiation showed that the final ratio of *trans*-butene/*cis*-butene approached the equilibrium value at 65° C, 0.726 (11). Even at these high conversions there was no evidence for the formation of heavier products and it may be assumed that the diiodobutane was not an important product.

Several series of experiments were done with constant iodine pressure and variable butene pressure, utilizing light from three spectral regions for production of iodine atoms: region (a) $\lambda > 5000$ Å; region (b) $\lambda < 5000$ Å; region (c) $\lambda = 2537$ Å. Only wavelengths transmitted by Pyrex were included in region (b). The two regions (a) and (b) correspond to the banded region and the continuum, respectively, of the iodine spectrum. In the banded region predissociation occurs, yielding two ground state atoms (12), while in the continuum direct dissociation gives one ground state, ${}^{2}P_{3/2}$, and one excited state, ${}^{2}P_{1/2}$, atom (13).

In regions (a) and (b) the initial rapid increase in the rate as the butene pressure was increased was followed by a much slower increase at higher butene pressures. Typical series of results are shown in Fig. 1(a, b, and c). A few series of experiments were done with constant butene pressure and variable iodine pressure, with incident light of wave-

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FIG. 1(a). Dependence of rate of isomerization on butene pressure at wavelengths > 5000 Å (temp. 54° C, iodine pressure 2 mm).
(b). Effect of nitrogen additions on the rate of isomerization at wavelengths > 5000 Å (temp. 65° C, iodine pressure 4 mm).
(c). Dependence of rate of isomerization on butene pressure at 4358 Å (temp. 65° C, iodine pressure 4 mm).

length greater than 5000 Å, one of which is shown in Fig. 2. In this case a limiting rate was reached at about 4 mm of iodine.

The dependence of the rate on the absorbed light intensity at various pressures of iodine and of butene is shown in Fig. 3(a-f). At high light intensities the rate was a linear function of the intensity, but in each case extrapolated to a small positive intercept.









In the banded region, using the mercury green line, 5461 Å, addition of butene or nitrogen to iodine caused an increase in the light absorbed by the iodine, as measured by the phototube. A maximum increase of about 28% was observed. The ratio of the absorption with added gas to the absorption with iodine alone as a function of added gas is shown in Fig. 4. This increased absorption is most probably the effect of pressure on



FIG. 4. Effect of additions of butene and nitrogen on light absorption by iodine in the banded region.

the width of the absorption band of the iodine molecule. Obviously such an effect would - not occur in a region of continuous absorption and indeed was not observed with light of wavelength less than 5000 Å.

Addition of nitrogen, on the other hand, did not appear to increase the concentration of iodine atoms in the banded region by increased predissociation of the iodine molecule (Fig. 1(b)). Pressures of up to 45 cm of nitrogen were added to 4 cm of butene and 2 mm of iodine, under which conditions the indirect effect of the nitrogen on the rate as a result of the increased light absorption by the iodine was almost within the experimental error in rate measurements. The rate of isomerization itself was not increased and in fact gradually decreased slightly, probably due to the effect of nitrogen as a third body in removing iodine atoms.

Oxygen caused a more pronounced drop in the rate of isomerization, but still a large excess (about 10 times that of butene) was required to decrease the rate by 25%. It seems likely that this decrease was again the result of removal of iodine atoms by recombination on oxygen, which might be much more efficient than recombination on nitrogen. With still greater pressures of oxygen, reactions with butene took place, but this aspect was not pursued further.

A series of experiments was done at a temperature of 98° C with 4 mm of iodine using light in the banded region. The rate of isomerization was increased by about a factor of three and approached a limiting rate higher than that at 65° C.

The Quantum Yield

Region (b)

The quantum yield measurements were made with light of wavelength 4358 Å since the potassium ferrioxalate solution absorbs too weakly at wavelengths greater than 5000 Å to permit a reliable measurement of the light intensity in that region. The average incident intensity at 4358 Å was 4×10^{19} quanta/min. Absorption by iodine at 4 mm was

16% or 6.6×10^{18} quanta/min. Using the values for the rate of isomerization shown in Fig. 1(c) a plot of $1/\phi$ against 1/p is shown in Fig. 5. From the intercept the upper limit



FIG. 5. Plot of the reciprocal quantum yield against reciprocal pressure at 4358 Å. (The data are from Fig. 1(c).)

of ϕ is seen to be approximately 0.1. The assumption is made, of course, that the primary quantum yield for production of iodine atoms is 2, but there seems little doubt of this for wavelengths less than 5000 Å. This very low value makes it at once apparent that the reaction is not a chain process with iodine atoms as the chain carriers, such as is observed in the similar reactions of bromine and chlorine atoms.

Region (c)

The few experiments done with the low-pressure mercury resonance lamp, region (c), are shown in Fig. 6. At 2537 Å the average total incident intensity was 3×10^{17} quanta/



FIG. 6. Dependence of rate of isomerization on butene pressure at 2537 Å (temp. 65° C).

min, with about 2×10^{16} quanta/min absorbed by 4 mm of iodine. Under these conditions of low light intensity absorbed the rate was a linear function of the butene pressure over the range of pressures studied.

DISCUSSION

Of the two possible species which may cause isomerization, an iodine atom or an excited iodine molecule, the former appears the more probable in the present system. Only light of wavelength greater than 5000 Å would form an excited iodine molecule with sufficient lifetime to undergo energy transfer. However, the similarity of the kinetics of isomerization with incident light of wavelength both above and below 5000 Å suggests that the same species is operative in both cases. Furthermore, addition of nitrogen, and oxygen, especially, would be expected to quench excited molecules more efficiently than is indicated by the results.

Mechanism of Isomerization

Regions (a) and (b)

In discussing the mechanism of isomerization of *cis*-butene by iodine atoms the following observations must be considered:

(a) The rate of isomerization was not first order with respect to butene.

(b) The rate was linearly dependent on the light intensity for high light intensities, extrapolating to a small positive intercept.

(c) The limiting quantum yield for isomerization was about 0.1.

The first result indicates that isomerization does not occur entirely by the simple addition of an iodine atom to *cis*-butene followed by dissociation of the radicals so formed to give a certain fraction, α , of *trans*-butene:

$$C + I \to R \tag{1}$$

$$R \rightarrow \alpha T + (1-\alpha)C + I,$$
 [2]

where C and T refer to *cis*- and *trans*-butene respectively. In this case the rate of isomerization would be a linear function of the butene pressure. However, if butene is also an efficient third body for recombination of iodine atoms, then an increase in butene pressure would have the effect of reducing the iodine atom concentration. If the rate of recombination is appreciable compared to the rate of isomerization, then the rate of isomerization will not increase linearly with butene pressure but will approach a limiting value.

$$\mathbf{R} + \mathbf{I} \to \alpha \mathbf{T} + (1 - \alpha)\mathbf{C} + \mathbf{I}_2$$
[2a]

The fact that the quantum yield approached a limiting value much less than 1 may be interpreted to mean that butene acts as a third body for the recombination of iodine atoms without necessarily undergoing isomerization. In other words the reaction of an iodine atom with butene does not always form a radical in which rotation about the C—C bond may occur. The interaction complex then must preserve the rigidity of the double bond and be sufficiently stable to allow recombination of iodine atoms by further reaction of the complex with another iodine atom. Such a structure may be a π -complex of an iodine atom with the double bond. These have been postulated (14) to occur in the recombination of iodine atoms with various third bodies and in the reaction of oxygen atoms and ozone with olefins (13).

$$C + I \rightarrow C:I$$
 [3]

$$C:I \to C + I$$
 [4]

$$C:I + I \to C + I_2$$
^[5]

The linear dependence of the rate of isomerization on the absorbed light intensity raises the problem of the order of the recombination reaction of iodine atoms in the present

system. In the flash photolysis experiments (14, 15) the rate of recombination of iodine atoms is second order in iodine atoms. In the present system the concentration of iodine atoms is less than that under the conditions of flash photolysis. Hence in this case, also, recombination will be second order in iodine atoms and the concentration of iodine atoms will depend on the square root of the absorbed light intensity. In order for the rate to appear linear with respect to light intensity under these conditions the rate of isomerization must also be second order in iodine atom concentration. Reactions [2] and [2a] will not give this dependence.

This situation will occur if isomerization proceeds not only by reactions [1] and [2] but by a certain fraction of the encounters represented by reaction [5]. If this reaction takes place by the simple abstraction of the iodine atom from the π -complex formed in [3] then isomerization would not be expected to occur. However, if 2,3-diiodobutane is formed as an intermediate, rotation about the C—C bond becomes possible and in the subsequent decomposition to butene and iodine isomerization may occur.

$$C:I + I \rightarrow CI_2$$

$$CI_2 \rightarrow \alpha T + (1 - \alpha)C + I_2$$
[6]
[7]

The linear dependence of the rate on the absorbed light intensity rules out the occurrence of isomerization by reaction [2a], which would lead to a dependence on the square root of intensity. Thus recombination of iodine atoms on butene appears to occur entirely by reactions [3], [4], [5], and [6]. This would suggest that the complex formed in [3] has a longer life than the radical formed in [1]. The heat of formation of the C_4H_8I radical may be very roughly estimated to be 25 kcal/mole.* With this value the radical is unstable toward the formation of butene-1 by 7 kcal/mole and slightly more for butene-2. On the other hand Christie *et al.* (15) have found values of a few kcal/mole for the heats of formation of several complexes formed by interaction of an iodine atom and a hydrocarbon molecule. Rand and Strong (16) also found a complex formation between iodine atoms and benzene when iodine was flash photolyzed in benzene solution. They found that the complex formed between iodine molecules and benzene. By analogy, the complex formed in [3] might well be more stable than the radical and have a lower energy barrier for formation.

If the mechanism of isomerization may be described by the following reactions,

$h\nu + I_2 \rightarrow 2I$	[Ia]
$I + C \rightarrow R$	[1]
$R \rightarrow \alpha T + (1-\alpha)C + I$	[2]
$I + C \rightarrow C:I$	[3]
$C:I \rightarrow C + I$	[4]
$C:I \rightarrow R$	[1a]
$C:I + I \rightarrow C + I_2$	[5]
$C:I + I \rightarrow CI_2$	[6]
$CI_2 \rightarrow \alpha T + (1-\alpha)C + I_2$	[7]
$I + I_2 \rightarrow I_3$	[8]
$I_3 \rightarrow I + I_2$	[9]
$I_3 + I \rightarrow 2I_2$.	[10]

*Values used in this estimation (17): $H_{125}(C_4H_{10}) = -29.8$; $D(sec-C_4H_9-H) = D(sec-C_3H_7-H) = 94$; $D(H_2) = 103.2$; $D(I_2) = 35.35$; $D(sec-C_4H_9-I) = 48$; $D(sec-C_4H_8I-H) = D(sec-C_4H_9-H)$.

the rate of isomerization (r_1) equals $\alpha[k_2(\mathbf{R})+k_7(\mathbf{CI}_2)]$. Therefore, for second-order atomic recombination (i.e. $k_9 \gg k_{10}(\mathbf{I})$ and $k_4 \gg (k_5+k_6)(\mathbf{I})$),

$$r_{1} = \frac{\alpha \left(k_{1} + k_{1a} \frac{k_{3}}{k_{4}}\right)(C) \sqrt{I_{a}}}{\sqrt{\left(k_{6} \frac{k_{3}}{k_{4}}\left(C\right)\right)} \sqrt{\left(\frac{k_{5} + k_{6}}{k_{6}} + \frac{k_{10} k_{3} k_{4}(I_{2})}{k_{6} k_{9} k_{3}(C)}\right)}} + \frac{\alpha I_{a}}{\frac{k_{5} + k_{6}}{k_{6}} + \frac{k_{10} k_{3} k_{4}(I_{2})}{k_{6} k_{9} k_{3}(C)}}$$

and

$$r_{1}(\%) = \frac{100\alpha \left(k_{1} + k_{1a}\frac{k_{3}}{k_{4}}\right) \sqrt{I_{a}}}{\sqrt{\left(k_{6}\frac{k_{3}}{k_{4}}(C)\right)} \sqrt{\left(\frac{k_{5} + k_{6}}{k_{6}} + \frac{k_{10}k_{8}k_{4}(I_{2})}{k_{6}k_{9}k_{3}(C)}\right)}} + \frac{100\alpha}{(C)} \times \frac{I_{a}}{\frac{k_{5} + k_{6}}{k_{6}} + \frac{k_{10}k_{8}k_{4}(I_{2})}{k_{6}k_{9}k_{3}(C)}}}$$

At constant pressures of C and I_2

$$r_{\rm i} = K_1 \sqrt{I_{\rm a}} + K_2 I_{\rm a}.$$

The intensity dependence plots (Fig. 3(a-f)) extrapolated to a small intercept and it may be seen that such behavior is consistent with this mechanism. Plots of $r_1/I_a^{\frac{1}{2}}$ against $I_a^{\frac{1}{2}}$ for each series of intensity dependence curves gave straight lines from which values for K_1 and K_2 were obtained. The ratio $(k_1k_4+k_{1a}k_3)^2/k_3k_4k_6$ was equal to the (intercept)²/ slope. Table I shows this ratio as well as values for K_1 , K_2 , $K_1I_a^{\frac{1}{2}}$, and K_2I_a for each series

TABLE I

Determination of the constants in the rate equation

I2 (mm)	Butene (mm)	I2 Butene	K_1	K_2	$K_1 \sqrt{I_a}$	$K_2 I_a$	$\frac{r_1+r_{1a}^*}{r}$	$\frac{r_6^*}{r}$	$\frac{\frac{(\text{intercept})^2}{\text{slope}}}{\frac{(k_1k_4+k_{1a}k_3)^2}{k_3k_4k_6}},$
$\begin{array}{c}2\\2\\2\\4\\4\\0.5\end{array}$	$\begin{array}{r} 4 \\ 60 \\ 110 \\ 10 \\ 90 \\ 4.5 \end{array}$	$\begin{array}{c} 0.50 \\ 0.033 \\ 0.0182 \\ 0.40 \\ 0.0445 \\ 0.111 \end{array}$	$\begin{array}{c} 0.24 \\ 0.10 \\ 0.081 \\ 0.155 \\ 0.195 \\ 0.068 \end{array}$	$\begin{array}{c} 1.50 \\ 0.235 \\ 0.125 \\ 0.460 \\ 0.246 \\ 0.110 \end{array}$	$\begin{array}{c} 0.0936\\ 0.0561\\ -0.0478\\ 0.122\\ 0.127\\ 0.0477\end{array}$	$\begin{array}{c} 0,228\\ 0.074\\ 0.0435\\ 0.285\\ 0.105\\ 0.0542 \end{array}$	$29.1 \\ 43.0 \\ 52.4 \\ 30.0 \\ 55.0 \\ 46.8$	$70.9 \\ 57.0 \\ 47.6 \\ 70.0 \\ 45.0 \\ 53.3$	$\begin{array}{c} 0.0384\\ 0.0429\\ 0.0525\\ 0.052\\ 0.154\\ 0.0416\end{array}$

 $*r_1, r_{1a}, r_6$, and r are, respectively, rates of reactions [1], [1a], [6], and the total isomerization.

of experiments covering a wide range of iodine and butene concentrations. The proportion of the isomerization which occurs by reactions [6] and [7] is greatest when the I_2 /butene ratio is largest. Absolute values for the ratio $k_{10}k_8k_4/k_6k_9k_3$ may not be obtained from these plots since only relative values for I_a were measured.

The observed dependence of the isomerization rate on the concentration of the reactants is qualitatively in agreement with the considered mechanism. A detailed quantitative treatment is precluded by the appreciable experimental scatter and by the complexity of the rate expressions. The proposed reaction mechanism is therefore of a tentative character. Both reactions [1] and [1a] have been included into the mechanism to show that the kinetic expressions are independent of whether the iodobutyl radicals (R) are assumed to be formed by direct addition of iodine atoms or by rearrangement of π -complexes (C:I).

Region (c)

Reactions [5] and [6] would be expected to be less efficient at low light intensities and

this is shown by the experiments using the mercury resonance line 2537 Å (Fig. 6). The light absorbed in this region was about 300 times less than that at 4358 Å. Although the points are scattered there appeared to be no curvature in the plot of rate against butene pressure. The quantum yield divided by the equilibrium trans/cis value reached unity at about 7 cm of butene and continued to increase as the butene pressure was increased. The rate of reaction [6] thus appears to be considerably reduced at these light intensities. At the same time, the more highly energetic iodine atom formed in this region may make reaction [1] much faster relative to [3].

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