Kinetics of the Gas-Phase Iodine-Catalyzed Isomerization of Methyl Acetylene and the Propargyl Stabilization Energy *

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The gas-phase iodine-catalyzed isomerization of methylacetylene to allene has heen investigated in the temperature range 280-330°C. The occurrence of side and secondary reactions precludes the observation of a simple rate expression. Arguments are presented favouring a mechanism involving

$$M+I_2 \Rightarrow M+2I$$

$$\mathbf{I} + \mathbf{C}\mathbf{H}_{3}\mathbf{C} \equiv \mathbf{C}\mathbf{H} \rightleftharpoons \mathbf{C}_{3}\mathbf{H}_{3} + \mathbf{H}\mathbf{I} \tag{1,-1}$$

$$C_{3}H_{3} + HI \rightarrow CH_{2} = C = CH_{2} + I$$
(2)

The data yield the following rate constant expression

 $\log \{k_1/(1+k_{-1}/k_2) \ \text{I. mol}^{-1} \ \text{s}^{-1}\} = (10.99 \pm 0.19) - (101.4 \pm 2.1 \ \text{kJ mol}^{-1})/2.303 \ \text{RT}$ from which is derived the bond dissociation energy, $DH^{\circ}(\text{H}-\text{CH}_2\text{CCH}) = 393 \pm 5 \ \text{kJ mol}^{-1}$ (93.9 kcal mol⁻¹) at 298 K. The propargyl radical C₃H₃ is stabilized by 17±5 kJ mol⁻¹ (4.1 kcal mol⁻¹).

The technique of catalysis by gas-phase iodine atoms has been extremely useful in establishing reliable values for bond dissociation energies and radical stabilization energies. The method, and the results obtained by it, have been recently reviewed.¹ Olefin isomerization studies ² have produced values for allylic and pentadienylic stabilization energies. No such studies have been performed with acetylenes.

The simplest stabilized acetylenic radical is propargyl (or propynyl) C_3H_3 , and estimates of its stabilization energy vary from >63.6³ to 40⁴ and ~25 kJ mol^{-1.5} These values were obtained by other methods and the present work was undertaken in order to establish a more precise figure.

EXPERIMENTAL

APPARATUS

This consisted of a static vacuum system, a stirred salt-bath thermostat and a gas chromatograph. The vacuum line was equipped with greaseless stopcocks (Springham) with Viton A diaphragms, apart from a section heated to ~100°C for the purposes of handling I₂ vapour, where conventional silicone greased taps were used. The Pyrex reaction vessel of ~300 ml capacity was coated with silicone oil DC703 to render the surface inactive,⁶ and connected to the vacuum system via a 3-way tap, the third arm of which was attached to a pressure transducer (Bell and Howell type 4–327–0003) which was also heated to ~100°C. Signals from the transducer were fed into a potentiometric recorder (Speedomax W). Pressure changes could be measured to an accuracy of ± 0.1 Torr.[†] A second reaction vessel

* A preliminary account of this work was reported at the Chemical Society meeting at Keele, 24-26 Sept., 1968.

 $1 \text{ Torr} = 133.3 \text{ N m}^{-2}$

packed with Pyrex tubes and similarly treated, having a surface-to-volume ratio 12-fold larger than the unpacked vessel was used in some experiments. Dead spaces were $\sim 1 %$ or less.

The stirred salt thermostat and temperature measuring devices were similar to those developed by Ellis and Frey.¹ Reaction vessel temperatures were uniform in both space and time to within $\pm 0.1^{\circ}$ C. Routine product analyses were performed on a Perkin Elmer gas chromatograph equipped with a flame ionization detector and gas sampling valve.

PROCEDURE

Prior to a kinetic run, iodine (at -20° C) and methylacetylene (at -196° C) were both degassed. I_2 was evaporated into the reaction vessel at a known pressure. A run was initiated when a known pressure of $CH_3C \equiv CH$ was then shared into the vessel. The pressure transducer was used to record initial and final pressures but not left continuously in contact with the reacting mixture because of small losses due to slow absorption of I_2 into the transducer. At the end of a run the contents of the vessel were expanded into a sample pipette via two traps, one maintained at $-18\pm3^{\circ}$ C to remove I₂ and the other containing solid glycine to remove HI. After isolation of the sample pipette the rest of the contents of the reaction vessel were pumped through the trapping system for ~ 1 min to recover the I₂ quantitatively.

ANALYSES AND PRODUCT IDENTIFICATION

Routine analyses of the contents of the sampling pipette were performed on two columns, (i) $3 \text{ m} \times 3 \text{ mm}$ of 20 % w/w bismethoxyethyl adipate on 60/80 Chromosorb P operated at room temperature with N₂ carrier gas at an inlet pressure of 11 p.s.i., and (ii) $4 \text{ m} \times 3 \text{ mm}$ of 15 % w/w polypropylene glycol LB 550X on 60/80 Chromosorb W operated at 60° C with N₂ carrier gas at an inlet pressure of 16 p.s.i. The former column was used for propylene, allene and methyl acetylene (analyses done in duplicate) and the latter for C_3 hydrocarbon (unresolved) and 2-iodopropene. The latter column, which separates most of the C_3 iodides, was also used qualitatively at 80°C and a carrier gas inlet pressure of 30 p.s.i. to detect the presence of C_3H_3I isomers. The flame detector was calibrated, with known mixtures of product and reactant vapours. Indine was analyzed by titration with $S_2O_2^{3-1}$ after its transfer from the -18° C trap. This procedure was carefully checked and essentially 100% recovery was possible.

2-Iodopropene was identified as a product, by allowing the side reaction which forms it to proceed to completion and recovering sufficient material for spectroscopic analysis. 3-Iodopropyne and iodoallene were identified as products by comparison of their retention times on column (ii) with those of a known mixture of the two compounds. They could not be analyzed quantitatively owing to adsorption losses in the trapping-out system.

MATERIALS

METHYL ACETYLENE (Matheson) was carefully purified to remove all traces (~ 0.5 %) of allene. A 2 l. bulb containing a crystal of I_2 was pressurized with cylinder methylacetylene The bulb was exposed to visible light from a 100 W W lamp (\sim 10 cm distant) to 0.5 atm. for 20 mins. The contents of the bulb (which now contained droplets of a colourless liquid) were transferred at -10° C to a vacuum line and distilled twice through traps at -78° C. V.p.c. analysis showed the following impurity levels: C_3H_6 (propylene) ~0.012 %, C_2H_2 ~0.1 %, C₃H₄ (allene) ~0.013 %, CH₃OCH₃ ~0.5 %, other (unidentified) ~0.3 %.

ALLENE. Samples were kindly provided by H. M. Frey and I. M. Mills. V.p.c. analysis showed the methyl acetylene content <0.015 % and total impurity <1 %.

2-IODOPROPENE. This was prepared by a procedure developed during the course of this research. Equal pressures of allene and HI were reacted together at 300°C in a Pyrex vessel for 5 min. The product was passed through the trapping system to remove I_2 and HI and into a trap at -78° C where it was pumped for 10 min. It was identified by mass spectrometry peaks at 168, 127, 41 and 39 a.m.u.; by n.m.r. absorptions at = 7.8, 4.6, 4.2τ

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(rel. H-counts 3 : 1 : 1 resp.) and by i.-r. absorptions at ~3100, 2970, 2930, 2860, 1790, 1625, ~1440, ~1385, 1160 and 897 cm⁻¹. The 897 cm⁻¹ is a type C band characteristic of an out-of-plane vibration of a =CH₂ group. This sample showed no evidence of impurities when analyzed by v.p.c. on column (ii).

3-IODOPROPYNE AND IODOALLENE. A mixture of these compounds was prepared by the reaction of 3-bromopropyne and sodium iodide.⁸ It was identified by n.m.r. as

ICH₂C==CH,

 $\tau = 7.2$ (triplet), 6.2 (doublet) (rel. H-counts 1:2); CH₂=C=CHI, $\tau = 5.3$ (doublet), 4.0 (triplet) (rel. H-count 2:1). The mixture contained ~60 % CH₂=C=CHI (by n.m.r.) and was sufficient to characterize column (ii) for v.p.c. analysis.

IODINE (Fisons) was resublimed before use and stored under vacuum.

HYDROGEN IODIDE solution (Fisons) was dropped on to P_2O_5 and the vapour evolved passed through a trap at -78° C before collection at -196° C. It was stored at room temperature in a blackened bulb and redistilled before use.

RESULTS

PRELIMINARY EXPERIMENTS

A series of experiments was performed at 330.7°C with initial partial pressures of 10 Torr of I_2 and 29.5 Torr of methyl acetylene (MA). Products which were identified and estimated quantitatively were allene, 2-iodopropene and propylene. Small peaks corresponding to 3-iodopropyne and iodoallene were observed but were not estimated quantitatively since it was discovered that their magnitude was affected by the presence of the solid glycine trap. The variation of product yields with reaction time is shown graphically in fig. 1. Allene is clearly a primary product but the curves



FIG. 1.—Major product formation in the reaction of I_2 (10.2 Torr) and MA (29.5 Torr) at 331°C: O, allene; \bigcirc , 2-iodopropene and \bigcirc , propylene.

for 2-iodopropene and propylene appear to approach t = 0 tangentially, which suggests that these products are secondary in nature. In addition, the reaction is accompanied by a pressure decrease and an iodine loss as indicated by the data shown in table 1 for the same set of runs.

These results indicate, by contrast with the I_2 catalyzed isomerization of the butenes,^{2a} a complex reaction system. The following stoichiometric reactions are consistent with these observations :

$$CH_3C \equiv CH \rightleftharpoons CH_2 \equiv C \equiv CH_2 \tag{A}$$

$$I_2 + MA \rightleftharpoons C_3 H_3 I + HI$$
 (B)

$$HI + C_3 H_4 \rightarrow CH_2 = CICH_3 \tag{C}$$

$$HI + CH_2 = CICH_3 \rightarrow C_3H_6 + I_2 \tag{D}$$

$$I_2 + MA \rightleftharpoons C_3 H_4 I_2$$
 (E)

Reactions (A) and (B) are processes expected for this system by analogy with similar studies. That reaction (A) only occurred in the presence of I_2 was confirmed by blank experiments with MA. Neither MA nor allene interconverted or pyrolyzed under the conditions of these experiments. Reaction (B) alone should produce only small quantities of C_3H_3I isomers since the equilibrium constant ¹ for similar such processes is typically $\sim 10^{-4}$. However, if HI is subsequently consumed by (C) and (D) larger quantities might accumulate as the reaction progresses. There was no evidence that this occurred.

Table 1.—Overall pressure and iodine concentration changes during reaction of I_2 (10.2 Torr) with MA (29.5 Torr) at 603.9 K

| time/min | $-\Delta P$ Torr | $-\Delta I_2$ Torr | | |
|----------|------------------|--------------------|--|--|
| 5 | 0.11 | 0.25 | | |
| 10 | 0.38 | 0.41 | | |
| 20 | 0.60 | 0.72 | | |
| 30 | 1.15 | 0.87 | | |
| 45 | 1.68 | 1.12 | | |
| 60 | 2.08 | 1.47 | | |

Several further experiments were conducted to test the reactions (C), (D) and (E). The results, briefly, were as follows. Reaction (C) was investigated by allowing HI to react with both MA and allene. The reaction with MA did form 2-iodopropene but was too slow to account for its formation in the system under study. The reaction with allene, on the other hand, was exceedingly rapid; when I_2 was present in addition the reaction was almost instantaneous. Reaction (C) is therefore most probably a reaction of allene.

Reaction (D) was also investigated separately and found to occur readily with propylene the major product. Its rate was consistent with its occurrence in the system under study. No direct analytical evidence was available for process (E) although several attempts were made to analyse the contents of the -18° C trap by u.v. spectroscopy for the presence of iodides. In one run (I₂ = 20 Torr, MA = 100 Torr) a weak absorption (after correction for I₂) at 260 ± 5 nm was observed. The principal argument for (E) rests on the analogous reaction between I₂ and acetylene known ⁹ to occur between 200 and 330°C.

If reactions (A)-(E) are the only processes occurring, the following conditions must be met :

$$-\Delta P = -\Delta [I_2] - [HI] = [C_3H_5I] + [C_3H_6] + [C_3H_4I_2],$$

where ΔP = pressure change, and ΔI_2 = iodine change. Provided [HI] is very small the first of these conditions is satisfied up to 30 min after which $-\Delta P > -\Delta I_2$, thereby indicating possible further side reactions. The second relationship may be used to

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obtain crude estimates of $[C_3H_4I_2]$. These are shown in table 2 and indicate that the diiodide reaches a stationary state. An equilibrium is expected, again by analogy with the I_2 + acetylene reaction, and the crude equilibrium constant which may be estimated from these data is close to a value calculated ¹⁰ from additivity rules.¹¹ This evidence argues strongly for the presence of the diiodide. The failure to detect it analytically is not serious, in view of the small quantities involved.

TABLE 2.—CALCULATED DIODIDE PRESSURES AND MASS BALANCES DURING REACTION OF I_2 (10.2 Torr) with MA (29.5 Torr) at 603.9 K

| time/min | [C ₃ H ₄ I ₂] Torr | mass balance | | |
|----------|------------------------------------------------------|--------------|--|--|
| 5 | 0.06 | 102 | | |
| 10 | 0.19 | 99 | | |
| 20 | 0.24 | 98 | | |
| 30 | 0.38 | 99 | | |
| 45 | 0.40 | 101 | | |
| 60 | 0,42 | 96 | | |

Also shown in table 2 are mass balances calculated on the assumption of complete stoichiometries (A)-(E) (i.e., with allowance for unmeasured C_3H_3I) using an absolute calibration of the analytical system reliable to within $\pm 4\%$. The good balances obtained indicate that no major product has been overlooked.

INITIAL RATE MEASUREMENTS

Kinetic studies were limited to the initial stages of reaction because of the rapid onset of secondary reactions. Fig. 2a and 2b show (product,time) curves up to 3 % conversion for two different sets of initial conditions. Even at low conversions 2iodopropene and propylene are formed. Although they still appear to be secondary products their rate of formation is clearly sufficiently fast to deplete the allene to some extent. Plots of the sum of these three products are approximately linear and as a consequence rates were subsequently obtained from single runs allowed to proceed to 1-2 % conversion. It was apparent from early experiments that initial rates showed a stronger dependence on MA than on I_2 concentration, and that these rates were approximately, but *not* exactly, first order in MA and half order in I_2 as has been found in other similar systems.¹

A detailed set of experiments at several temperatures was carried out where the MA initial pressure was varied between 6 and 100 Torr and the I_2 initial pressure between 3 and 20 Torr. The ratio [MA]/[I_2] was varied by a factor of 100 and an apparent rate constant k calculated on the assumption that

$d\Sigma[\text{allene} + C_3H_5I + C_3H_6]/dt = k[I_2]^{\frac{1}{2}}[\text{MA}].$

The results of these studies are shown in table 3. The values for k at a given temperature vary, in some cases, over a range of ± 20 % from the mean. A trend toward higher values of k at higher values of $[MA]/[I_2]$ is discernible. Plots of k against $[MA]/[I_2]$ unfortunately show too much scatter to indicate their form. Several runs were performed in the packed vessel to test whether this effect could be attributed to a surface process. These results are also shown in table 3. Reaction rates and values of k were not significantly different, although secondary formation of 2-iodopropene and propylene at the expense of allene was greater. It is concluded that surface effects are unimportant for the primary process. The observed variations of k can be shown to arise from a failure of an intermediate to reach a rapid stationary concentration in the mechanism proposed. This is discussed later and shown to be



FIG. 2.—Product formation in the early stages of reaction: ○, allene; ④, 2-iodopropene; ● propylene and x, total = [allene]+[C₃H₅I]+[C₃H₆].
(a) at 300°C, [I₂] = 20.4 Torr, [MA] = 98 Torr.
(b) at 331°C, [I₂] = 3.4 Torr, [MA] = 6.9 Torr.

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TABLE 3

| reactant | | | | [product]/[MA]×10 ² | | | | | |
|--------------------------|------------|-------------|--------------|--------------------------------|----------------|---------------------------------|--------------|-------------------------------------------|----------------------------------------------------|
| temp. ^a °C | I2 Torr | MA Torr | time mins | C ₃ H ₆ | allene | C ₃ H ₅ I | Σ^{b} | [I ₂] _{av} c Torr | 103 <i>k</i> Torr ^{-‡} s ⁻¹ |
| 279.8 | 10.1 | 10.0 | 100 | 0.071 | 0.746 | 0.411 | 1.228 | 9.6 | 0.0396 |
| 279.8 | 5.21 | 49.8 | 150 | 0.065 | 0.847 | 0.337 | 1.249 | 4.63 | 0.0387 e |
| 279.8 | 3.50 | 10.5 | 180 | 0.059 | 0.953 | 0.261 | 1.273 | 3.36 | 0.0386 |
| 279.8 | 20.1 | 6.4 | 70 | 0.056 | 0.730 | 0.261 | 1.047 | 19.6 | 0.0338 |
| 279.8 | 20.5 | 48.8 | 70 | 0.064 | 0.668 | 0.376 | 1.108 | 18.7 | 0.0366 |
| 280.8 | 20.1 | 51 1 | 25 | 0.068 | 0 722 | 0 201 | 1 001 | 10.0 | 0.0715 |
| 207.0 | 20.1 | 76 | 25 | 0.000 | 0.722 | 0.301 | 1.091 | 19.0 | 0.0713 |
| 207.0 | 5 50 | 50.1 | 33 75 | 0.009 | 0.717 | 0.301 | 1 2 2 2 | 5.05 | 0.0099 |
| 207.0 | 10.2 | 10.0 | 50 | 0.005 | 0.965 | 0.275 | 1.525 | 5.05 | 0.0763 * |
| 207.0 | 10.2 | 10.0 | 20 | 0.033 | 0.000 | 0.201 | 1.004 | 2.0 | 0.0080 |
| 209.0 | 4.02 | 10.0 | 80 | 0.001 | 0.932 | 0.151 | 1,104 | 5.65 | 0.0745 |
| 299.8 | 20.4 | 97.8 | | | | | | | 0.116 ^d |
| 299.8 | 3.48 | 6.8 | | | | | | | 0.124 ď |
| 299.8 | 20.3 | 6.2 | | | | | | | 0.112 d |
| 299.8 | 3.40 | 96.4 | 45 | 0.056 | 0. 9 53 | 0.188 | 1.197 | 2.98 | 0.154 |
| 299.8 | 5.68 | 51.2 | 35 | 0.068 | 0.969 | 0.229 | 1.266 | 5.37 | 0.156 e |
| 299.9 | 21.5 | 6.7 | 20 | 0.047 | 0.817 | 0.132 | 0.996 | 21.5 | 0.108 |
| 299.8 P | 10.3 | 11.8 | 30 | 0.069 | 0.640 | 0.490 | 1.199 | 9.7 | 0.129 |
| 299.8P | 28.9 | 8.5 | 17 | 0.058 | 0.609 | 0.479 | 1.146 | 28.1 | 0.127 |
| 299.8 P | 5.4 | 52.7 | 45 | 0.103 | 0.940 | 0.605 | 1.648 | 4.8 | 0.167 |
| 299.8 P | 21.2 | 53.0 | 20 | 0.082 | 0.668 | 0.259 | 1.009 | 19.4 | 0.115 |
| 310.0 | 10.1 | 11 2 | 15 | 0 136 | 0 975 | 0 185 | 1 296 | 99 | 0.275 |
| 310.0 | 20.1 | 6.6 | 10 | 0.150 | 0.762 | 0.105 | 0 944 | 20.1 | 0.213 |
| 310.0 | 3.47 | 11.6 | 30 | 0.125 | 1.279 | 0.156 | 1.560 | 3 47 | 0.279 |
| 310.0 | 20.4 | 54.5 | 10 | 0.056 | 0.874 | 0.201 | 1.140 | 19.6 | 0.258 |
| 310.0 | 5.49 | 51.2 | 25 | 0.084 | 1.278 | 0.217 | 1.579 | 5.22 | 0.276 |
| 200 Q D | 5 71 | 547 | 20 | 0.075 | 0.045 | 0 242 | 1 262 | 5 76 | 0.208 |
| 200.0P | 20.2 | 54.1 6.9 | 15 | 0.075 | 0.945 | 0.343 | 1.505 | 10.0 | 0.290 |
| 309.9 F | 20.2 | 0.0 | 15 | 0.140 | 0.005 | 0.042 | 1.435 | 19.9 | 0.210 |
| 319.8 | 20.1 | 52.3 | 6 | 0.038 | 0.965 | 0.154 | 1.157 | 19.5 | 0.437 |
| 319.8 | 10.3 | 11.7 | 8 | 0.012 | 0.862 | 0.049 | 0.923 | 10.2 | 0.362 |
| 319.8 | 3.28 | 11.5 | 15 | 0.013 | 1.056 | 0.054 | 1.123 | 3.18 | 0.420 |
| 319.8 | 5.62 | 50.7 | 12 | 0.040 | 1.213 | 0.137 | 1.390 | 5.40 | 0.498 e |
| 319.7 | 20.1 | 8.1 | 6 | 0.075 | 0.852 | 0.079 | 1.006 | 20.1 | 0.374 |
| 330.6 | 3 30 | 973 | | | | | | | 0 905 d |
| 330.6 | 20.5 | 65 | | | | | | | 0.729 4 |
| 330.6 | 3 37 | 69 | | | | | | | 0.721 d |
| 330.6 | 20.5 | 98.5 | | | | | | | 0 733 d |
| 330.5 | 5 80 | 51.0 | 7 | 0.035 | 1 328 | 0 105 | 1 468 | 5 70 | 0.877 |
| 330.3 | 5.65 | 51.6 | , 8 | 0.069 | 1.508 | 0.184 | 1.761 | 5.54 | 0.930 |
| 330.3 | 5.80 | 51.2 | Ř | 0.067 | 1.489 | 0.186 | 1.742 | 5.61 | 0.920 . |
| 330.3 | 21.0 | 6.8 | 5 | 0.063 | 1.310 | 0.108 | 1.481 | 21.0 | 0.646 |
| | | | - | | | | | | |

^a P indicates run performed in the packed vessel; $b\Sigma = [C_3H_6] + [allene] + [C_3H_5I]$; $c[I_2]_{av} = [I_2]_0 - \frac{1}{2}\Delta I_2$; ^d these rate constants were obtained from the slopes of product time plots (such as those in fig. 2a and 2b); ^e these results only used in the restricted Arrhenius plot.

least serious at high $[MA]/[I_2]$. For this reason two Arrhenius plots of the data in table 3 have been made. One included all values of k listed and a least-squares analysis gave

$$\log (k/\text{Torr}^{-\frac{1}{2}} \text{s}^{-1}) = (9.597 \pm 0.301) - (167.28 \pm 3.33 \text{ kJ mol}^{-1})/2.303 \text{ }RT$$

The other only included the value of k at the highest value of the ratio $[MA]/[I_2] (\simeq 10)$ at each of six temperatures and a least-squares analysis gave

 $\log (k/\text{Torr}^{-\frac{1}{2}} \text{s}^{-1}) = (10.146 \pm 0.189) - (172.81 \pm 2.09) \text{ kJ mol}^{-1}/2.303 \text{ RT}$

DETERMINATION OF THE BOND DISSOCIATION ENERGY

The following mechanism is proposed by analogy with the iodine-catalyzed positional isomerization of 1-butene 2^a and the reaction of iodine with hydrocarbons 1 in general, to account for the overall processes (A) and (B):

$$I_2(+M) \rightleftharpoons 2I + (M)$$
 K_{I_2}

$$\mathbf{I} + \mathbf{C}\mathbf{H}_{3}\mathbf{C} \equiv \mathbf{C}\mathbf{H} \rightleftharpoons \mathbf{C}_{3}\mathbf{H}_{3} + \mathbf{H}\mathbf{I}$$
(1)

$$C_3H'_3 + HI \rightarrow CH_2 = C = CH_2 + I^{\bullet}$$
(2)

$$C_3H_3 + I_2 \rightleftharpoons C_3H_3I + I. \tag{3}$$

The C_3H_3 is the propargyl (propynyl) radical and C_3H_3I formed in (3) will be a mixture of propargyl iodide and iodoallene. If steps (3) and (-3) are at equilibrium a stationary state treatment of this mechanism leads to

$$\frac{d[allene]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} K_{1_2}^{\frac{1}{2}} [I_2]^{\frac{1}{2}} [CH_3 C \equiv CH].$$

If steps (3) and (-3) are not at equilibrium the rate of allene formation will be less than that given by the above expression since $C_3H_3^{-}$ is being depleted by another pathway. The iodide forming reactions in these systems ^{1, 2} usually reach equilibrium rapidly and at low conversions, but because the onset of secondary reactions restricted the study of this system to low conversions, the possibility that equilibrium was not reached had to be examined. In the appendix it is shown that the perturbing influence of (3) and (-3) on the initial rate of allene formation depends on the value of $[MA]^{\frac{1}{2}}/[I_2]^{\frac{1}{2}}$ and is least where this ratio is high. The experimental increase of k with $[MA]/[I_2]$ is consistent with this prediction. The trend of k with $[MA]/[I_2]$ is not strong and this, taken together with the fact that the experimental orders in [MA]and $[I_2]$ are close to one and one half respectively, suggests that at the highest value of $[MA]/[I_2]$ ($\simeq 10$), the limiting approximation $k = k_1k_2 K_{I_2}^{\frac{1}{2}}/(k_{-1}+k_2)$ is reached. From the experimental Arrhenius expression for k under these conditions and the known values of $K_{I_2}^{\frac{1}{2}}$, the following expression was obtained,

log
$$\{k_1/(1+k_{-1}/k_2) \ \text{I. mol}^{-1}\ \text{s}^{-1}\} = (10.99 \pm 0.19) - (101.4 \pm 2.1 \ \text{kJ mol}^{-1})/2.303 \ \text{RT}$$

The value of k_{-1}/k_2 is unknown. Solution studies of the reactions of the C₃H₃ radical have indicated that it produces five times more methyl acetylene than allene in abstraction from (n-Bu)₃SnH. The present system is studied under different conditions, however, and in the fast abstraction reactions of radicals ¹ with HI, rates are comparable for many radicals. In the absence of a value, we prefer to assume that $k_{-1}/k_2 = 1$ and $E_1 - E_2 = 0$. This then leads to,

$$\log (k_1/l. \text{ mol}^{-1} \text{ s}^{-1}) = (11.29 \pm 0.19) - (101.4 \pm 2.1 \text{ kJ mol}^{-1})/2.303 \text{ RT}.$$

If it is further assumed that $E_{-1} = 5 \pm 4 \text{ kJ mol}^{-1}$, again by analogy with other radicals,¹ then

$$\Delta H_{1,-1}(578 \text{ K}) = 96.4 \pm 5 \text{ kJ mol}^{-1}$$

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Correction of this enthalpy change to room temperature using $\overline{\Delta C_p^{\circ}} = 6.53 \text{ J mol}^{-1}$ K⁻¹, estimated by the methods proposed by Benson ¹⁴ yields

$$M_{1,-1}^{\circ}(298 \text{ K}) = 94.6 \pm 5 \text{ kJ mol}^{-1}$$

From literature values for the heats of formation of I,¹² HI,¹² and MA,¹⁵

 $\Delta H_f^{\circ}(C_3H_3,g) = 360.5 \pm 5 \text{ kJ mol}^{-1}.$

This value leads directly to

 $DH^{\circ}(\text{HC} \equiv \text{CCH}_2 - \text{H}) = 393.1 \pm 5 \text{ kJ mol}^{-1} (93.9 \text{ kcal mol}^{-1}).$

Compared with the standard primary C—H bond dissociation energy of 410 kJ mol⁻¹,¹⁶ this value is less by 17 ± 5 kJ mol⁻¹. This is the stabilization energy of the propargyl radical.

DISCUSSION

KINETICS AND MECHANISM

This reaction system is considerably more complex than that for olefin isomerization. Reactions (A) and (B) have their analogues in the latter systems, and reaction (E) is paralleled in the $I_2 + C_2H_2$ system.⁹ The kinetics and mechanism of (A) and (B) have already been discussed. We note that the *A* factor for step (1), $10^{11.3}$ l. mol⁻¹ s⁻¹ reasonable value for such a process. Other iodine-atom-abstraction *A* factors lie in the range $10^{10.9}$ - 10^{12} l. mol⁻¹ s⁻¹ where unstabilized radicals are formed, and $10^{8.4}$ - $10^{10.2}$ l. mol⁻¹ s⁻¹ where stabilized radicals are produced. The propargyl radical is stabilized, but unlike other stabilized radicals its formation leads to no loss of internal rotational modes by comparison with the parent hydrocarbon. Thus, an *A* factor more appropriate to the formation of an unstabilized radical is to be expected.

No detailed results were recorded for reactions (C)-(E) and so their mechanisms remain unclear. The choice lies in each case between radical and molecular pathways, and although no clear-cut decisions can be made it is likely that the radical pathway in (C) is extremely rapid due to occurrence of the exothermic addition step

 $I + CH_2 = C = CH_2 \rightarrow CH_2 - CH_2 - CH_2$

 $(\Delta H^{\circ} \sim -62 \text{ kJ mol}^{-1})$ followed by the exothermic abstraction

 $CH_2 \cdots CI \cdots CH_2 + HI \rightarrow CH_2 = CICH_3 + I^{\bullet}$

 $(\Delta H^{\circ} \sim -71 \text{ kJ mol}^{-1}).$

STABILIZATION ENERGY OF PROPARGYL

The value of 17 ± 5 kJ mol⁻¹ is less than that obtained by other workers.³⁻⁵ The electron impact data of Collin and Lossing ³ suggested a value >63.6 kJ mol⁻¹. The uncertainties of electron impact ¹⁶ are illustrated by the fact that Collin and Lossing ¹⁷ previously obtained a value for the allyl stabilization energy which was ~38 kJ mol⁻¹ higher than the currently accepted value.¹ In a solution study, Martin and Sanders ⁵ obtained a difference between allylic and propargylic stabilization energy is fully released in the transition state. This would imply a propargyl stabilization of ~25 kJ mol⁻¹. This is in tolerable agreement with the present result, despite the differences in reaction systems and conditions.

Wing Tsang⁴ has obtained a value of $\sim 40 \text{ kJ mol}^{-1}$ from a shock tube study of the decomposition of 4-methyl-1-pentyne. Two factors which probably contribute to the discrepancy between this and the present work are compensation of Arrhenius parameters and inaccurate assumptions about the rate constants of back reactions.

The A factor for 4-methyl-1-pentyne fragmentation is $10^{15.56}$ s⁻¹ which is reasonable for such a process.¹⁸ Nevertheless, both this figure and the A factor in the present work might be in error by up to a factor of 10. If this were so for both reactions, then compensation in experimental activation energies could remove the discrepancy. As far as the back reactions are concerned, rate constants both in this work and Wing Tsang's are estimated by analogy with those for similar processes. In Wing Tsang's case, however, the appropriate back reactions are radical recombination processes. The assumption has always been that $E_a = 0$ for such processes (at all temperatures) but ¹⁸ this leads to irreconcilable values for $k_{dissociation}/k_{recombination}$ and $\bar{K}_{equilibrium}$ for some dissociation processes.¹⁹ This difficulty may be exacerbated by the lengthy extrapolation from temperatures of the shock tube study (1100 K) to room tempera-For this reason, it is believed that the value of $17+5 \text{ kJ mol}^{-1}$ represents a ture. better estimate of the propargyl stabilization energy than has been available hitherto.

So far, it has been tacitly assumed that the propargyl stabilization energy has a unique value. However, since the propargyl radical may also be derived from allene an alternative definition exists. The experimental result for $\Delta H^{\circ}(C_3H_3,g)$ taken with the literature value for ΔH_{ℓ}° (allene) ¹⁵ yields

$$DH^{\circ}(CH_2 = C = CH - H) = 386.4 \pm 5 \text{ kJ mol}^{-1}.$$

This may be compared with the standard C_{sp^2} -H bond dissociation energy ¹ (as in C_2H_4) of ≥ 452 kJ mol⁻¹. This would imply a stabilization energy of ≥ 66 kJ mol⁻¹. This value differs from the other because of the different π bond systems of the two parent hydrocarbons. The difference of 49 kJ mol⁻¹ represents the difference in energy between the second π bond in methyl acetylene and the second (strained) π bond in allene. Either definition is permissable but the former is usually used. However, if the propargyl stabilization energy is to be treated as a transferable quantity care must be taken to use the appropriate definition. Previous workers have speculated upon the origin of propargyl resonance energy.³⁻⁵ The radical is a resonance hybrid of the two valence bond forms $\dot{C}H_2$ — $C \equiv CH \leftrightarrow CH_2 = C = \dot{C}H$. Since these forms are different, mixing of their structures should lead to less stabilization than in cases, such as allyl, where the valence bond forms are the same.

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APPENDIX

CALCULATION OF THE PERTURBING EFFECT OF IODIDE FORMATION UPON THE RATE OF ISOMERIZATION OF METHYL ACETYLENE

The precise stationary state treatment of reactions (1), (-1), (2), (3) and (-3) is complex and involves the solution of coupled differential equations. This problem may be solved approximately as follows. First, iodide formation is treated in the absence of isomerization step (2). This gives an unperturbed "half life" for iodide formation. Secondly, an " unperturbed reaction time" for isomerization in the absence of iodide formation is ob-A comparison of these two times will then indicate the extent of interference of the tained. two processes with one another.

(i) HALF LIFE FOR IODIDE FORMATION ALONE (steps (1), (-1), (3), (-3)). The stationary state treatment gives,

$$\frac{d[RI]}{dt} = \frac{k_1[I][MA]}{1+k_{-1}[HI]/k_3[I_2]} \left\{ 1 - \frac{[RI][HI]}{[I_2][MA]} \frac{1}{K} \right\},$$

where $R \equiv C_3H_3$ and $K = [HI]_e[RI]_e/[I_2]_e[MA]_e$, the equilibrium constant for iodide formation. Since typically ${}^{1} K \sim 10^{-4}$, and $k_3 \gg k_{-1}$, this may be simplified to

$$\frac{\mathrm{d}[\mathrm{RI}]}{\mathrm{d}t} = k_1 [\mathrm{I} \cdot] [\mathrm{MA}]_0 \left\{ 1 - \frac{[\mathrm{RI}][\mathrm{HI}]}{[\mathrm{I}_2][\mathrm{MA}]_0} \frac{1}{K} \right\}$$

This equation has the form $dx/dt = c(1-x^2/x_e^2)$, where x = [RI] = [HI], $x_e = [RI]_e = [HI]_e = [HI]_e = [I_2]_0[MA]_0K^{\frac{1}{2}}$ and $c = k_1[I\cdot][MA]_0$. The half-life $t_x(x/x_e = \frac{1}{2})$ is found by integration to be given by,

$$t_{x} = \frac{x_{e}}{2c} \ln 3 = \frac{K^{\frac{1}{2}} [I_{2}]_{0}^{\frac{1}{2}}}{2k_{1} [I \cdot] [MA]^{\frac{1}{2}}} \ln 3.$$
(4)

(ii) REACTION TIMES FOR ISOMERIZATION ALONE (steps (1), (-1), (2)). The stationary state treatment gives

$$d[allene]/dt = k_1[I^{-}][MA]/(1+k_{-1}/k_2)$$

Typical low conversions in these experiments are 1 %, i.e.,

 $[allene]/[MA] \sim 10^{-2}.$

If Δt is the time for 1 % reaction

:
$$10^{-2}/\Delta t = k_1[I.]/(1+k_{-1}/k_2)$$

and

$$\Delta t = 10^{-2} \left(1 + k_{-1}/k_2 \right) / k_1 [I_{\cdot}].$$
⁽⁵⁾

Comparing eqn (4) and (5), therefore

$$\frac{\Delta t}{t_x} = 10^{-2} \frac{1 + k_{-1}/k_2}{K^{\frac{1}{2}} \ln 3} \frac{[\text{MA}]^{\frac{1}{2}}}{[\text{I}_2]_0^{\frac{1}{2}}}.$$

Thus, assuming $k_{-1}/k_2 = 1$ and since $K \sim 10^{-4}$,

$$\Delta t/t_x \sim 4[MA] \frac{1}{2} [I_2] \frac{1}{2}$$

Only if $\Delta t \ge t_x$ will iodide formation (which will essentially be complete) not interfere with the kinetics of allene formation. This condition is not satisfied in these experiments except perhaps at the highest values of $[MA]_0/[I_2]_0$.

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