of the spectra of the two symmetrical isomers with peaks at δ 5.12 (q, 2, $J \sim 7$ Hz with further fine splitting), 1.42–1.75 (m, 12); ir (CS_2) 815, 835, 875, 945, 1000, 1030, 1040, 1055, and 1085 cm^{-1}; the uv spectrum showed only end absorption λ (ethanol) 230 mμ (ϵ 2900).

trans,trans-**3,4-Dimethyl-2,4-hexadiene** was prepared by thermal decomposition of 2-butenylsilver(I) and purified by glpc (column C).[79] Its structure was assigned on the basis of spectra and analysis, and by elimination of the cis,trans and cis,cis isomers as possible structures: nmr (CCl_4) δ 5.48 (q, 2, $J = 6.5$ Hz), 1.72 (s, 6), and 1.67 (d, 6, $J = 6.5$ Hz); ir (CS_2) 810, 1020, 1070 cm^{-1}; uv, end absorption λ (ethanol) 230 mμ (ϵ 1200).

Anal. Calcd for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 87.07; H, 12.82.

Reactions of ***trans*-Propenyllithium with Transition Metal Halides.** The same general procedure was used for each reaction. Anhydrous transition metal halide (50–100 mg) was transferred into a tared flame-dried 12-ml stoppered centrifuge tube in a nitrogen-filled glove bag, the tube was removed from the bag, and the weight of the salt determined by weighing the tube. The tube was flushed with nitrogen, the salt suspended in ether or THF ($\sim$2–10 ml, sufficient to result in a solution $\sim$0.1 *M* in metal ion), and the suspension cooled to −78°. A measured volume of an ether solution of *trans*-propenyllithium ($\sim$0.1–0.2 *N*) containing *n*-decaneas internal glpc standard was transferred by forced siphon through a cannula into the suspension of transition metal salt. The centrifuge tube containing the reaction mixture was shaken or stirred at −78° for 5–15 min, then allowed to stand at room temperature for 6–18 hr. The reaction mixtures were usually hydrolyzed with 0.2 ml of water before analysis by glpc on column C.

Reduction of 2-Bromo-2-butene with Tri-*n*-butyltin Hydride. *cis*-2-Bromo-2-butene (0.883 g, 6.54 mmol, 91% cis), *cis*-2-pentene (Phillips Petroleum, 0.170 g, 95% cis), and *n*-heptane (0.212 g, glpc internal standard) were placed in a 5-ml flask. Samples could be taken by inserting a syringe needle through a serum stopper and a stopcock connected to the flask. Tri-*n*-butyltin hydride[80] (2.247 g, 7.72 mmol) was added to the *cis*-2-bromo-2-butene by syringe. No effort was made to flush air from the system whose dead volume was *ca.* 4 ml.

Samples were withdrawn at intervals and analyzed on either column C at 65° or on a 6-ft 10% benzylnitrile–silver nitrate column[81] at −15°. After 1 hr, the cis–trans ratio of 2-butenes formed was 33.5:66.5. After 17 hr, 48% of *cis*-2-bromo-2-butene had been converted to 2-butene with a 33.5:66.5 cis–trans ratio, and 45% of the *cis*-2-bromo-2-butene (86% cis) had not reacted. After 2-hr reaction, the cis–trans ratio of 2-pentene was still 95:5.

Similarly, *trans*-2-butene (1.077 g, 7.98 mmol, >99% trans) was reduced with tri-*n*-butyltin hydride (2.255 g, 7.75 mmol) at room temperature in the presence of *cis*-2-pentene (0.109 g, 95% cis) and *n*-heptane (0.155 g, glpc internal standard). After 1 day, 28% of the *trans*-2-bromo-2-butene had been converted to a 36:64 mixture of *cis*- and *trans*-2-butene, while 69% of the *trans*-2-bromo-2-butene had not reacted. Neither *trans*-2-bromo-2-butene nor *cis*-2-pentene were isomerized under the reaction conditions after 1 day.

Reaction of Tri-*n*-butyltin Hydride with *cis*-2-Butenyl(tri-*n*-butylphosphine)copper(I). A 0.15 *N* solution of *cis*-2-butenyl(tri-*n*-phosphine)copper(I) (0.96 mmol) from which lithium halide had been removed as a dioxane precipitate was cooled to −78° and tri-*n*-butyltin hydride (200 μl; 0.756 mmol) was added to give a deep red solution. Upon warming to room temperature, the solution became black. *n*-Heptane and *n*-decane were added to the decomposed solution for use as glpc standards. The solution was analyzed by glpc on column C and on a 6-ft 10% benzylnitrile–silver nitrate column. The products were 2-butene (0.38 mmol, 40% yield, 78% cis) and *cis,cis*-2,4-hexadiene (0.05 mmol, 11% yield).

In a similar reaction, *cis*-2-butenyl(tri-*n*-butylphosphine)copper(I) (0.84 mmol), tri-*n*-butyltin hydride (0.76 mmol), and *trans*-2-bromo-2-butene (0.96 mmol) were mixed at −78° and warmed to room temperature for several hours. Analysis showed that the solution contained 2-butene (0.40 mmol, 47% yield, 66% cis), 3,4-dimethyl-2,4-hexadienes (0.05 mmol, 12% yield, 85% cis isomeric purity), and *trans*-2-bromo-2-butene (0.83 mmol).

Acknowledgments. We wish to express our appreciation to Dr. H. L. Mitchell for running mass spectra, and to Drs. W. A. Sheppard and A. Cairncross for informing us of many of their results prior to publication.

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[79] The glpc retention times of the three isomeric 3,4-dimethyl-2,4-hexadienes on this column at 30° under comparable conditions were: trans,trans, 8.6 min; cis,trans, 12.2 min; cis,cis, 27.0 min.

[80] G. J. M. Van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, 7, 366 (1957).

[81] F. van de Craats, *Anal. Chem. Acta*, **14**, 136 (1956).

Reactions of Iodine with Olefins. I. Kinetics and Mechanism of Iodine Addition to Pentene Isomers[1]

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Abstract: The kinetics of the addition of iodine to 1-pentene, *cis*- and *trans*-2-pentenes, 2-methyl-1-butene, and 2-methyl-2-butene have been studied using ^{131}I-labeled iodine. The data support the view that the stereospecific addition is the result of an attack of an iodine atom or molecule on a charge-transfer complex between the olefin and the corresponding iodine molecule or atom. For 1-pentene at 25° it was found that the charge-transfer equilibrium constant K_c is 1.0×10^{-1} mol^{-1} l. The rate constant, k_1, for the reaction of the iodine atom or molecule with the complex was found to be 2.38×10^{-1} min^{-1} mol$^{-1/2}$ l.$^{1/2}$. It was also found that the vicinal diiodides, the products of the addition, were reasonably stable in the dark, if care was taken to remove all excess iodine.

Sumrell, *et al.*,[2] and Skell and Pavlis[3] have reported that, contrary to information commonly found in the literature,[4–7] iodine readily adds to 1-pentene and C_4 alkenes, respectively. They reported that in the liquid phase and ordinary room illumination the reac-

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[1] This research was supported through an Atomic Energy Commission Contract, No. AT(11-1)-1617. This is AEC Document COO-1617-23.

[2] G. Sumrell, B. M. Wyman, R. G. Howell, and M. C. Harvey, *Can. J. Chem.*, 42, 2710 (1964).

[3] P. S. Skell and R. R. Pavlis, *J. Amer. Chem. Soc.*, **86**, 2956 (1964).

[4] T. S. Paterson and J. Robertson, *J. Chem. Soc.*, **125**, 1526 (1924).

[5] A. Fairbourne and D. W. Stevens, *ibid.*, 1973 (1932).

[6] M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, 79, 1701 (1957).

[7] F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 (1958).

tion proceeds *via* a mildly exothermic reaction which goes essentially to completion.

$$RCH{=}CHR' + I_2 \longrightarrow RCHICHIR'$$

In their study of the addition–elimination cycle of iodine to *cis*- and *trans*-2-butenes, Skell and Pavlis[3] proposed a radical chain mechanism, proceeding *via* a bridged radical intermediate. The basis for their hypothesis was the observed photoacceleration and stereospecific nature of the addition–elimination reactions of iodine with the corresponding 2-butenes.

Benson, *et al.*,[8] have shown that the I-atom-catalyzed elimination of iodine from vicinal diiodides must be a concerted process, proceeding by a single-step elimination. They further concluded that if the decomposition reactions are concerted processes, then, by the principle of microscopic reversibility, the addition reactions also must be concerted processes. However, this microscopic reversibility argument has been challenged for reasons discussed by Burwell and Pearson.[9]

This controversy over the sequence of formation of the transition state has been summarized by Noyes, *et al.*[10] No conclusion could be reached concerning the existence of the bridged radical intermediate proposed by Skell and coworkers[3,11,12] to explain several of these results.

Because of the widespread use of iodine as a radical scavenger, particularly in radiolysis studies where olefins are commonly produced, and in view of the uncertainty in the rate and mechanism of addition of iodine to unsaturated hydrocarbons, we have investigated the kinetics of the addition of iodine to various C_5 alkene isomers in solution at 25° in an effort to shed additional light on the mechanism of the reaction.

Experimental Section

Materials. The olefins employed in this study (**1-pentene, *cis*-** and ***trans*-2-pentene, 2-methyl-2-butene,** and **2-methyl-1-butene**) were Phillips research grade materials, which were stated to be 99.53% pure. They were used without further purification. Iodine (Baker reagent grade) was sublimed before use. All the other chemicals were reagent grade and were used without further purification.

Radioactive iodine was used in the kinetic experiments. Solution of the tagged iodine was prepared by oxidizing with H_2O_2, an aqueous solution of $Na^{131}I$ (approximately 10 mCi) containing some nonactive NaI as carrier. The reaction was catalyzed by trace amounts of HNO_3. The iodine formed was immediately extracted into carbon tetrachloride. The concentration of iodine in CCl_4 was determined spectrophotometrically. The final solution of ^{131}I-tagged iodine in CCl_4 contained 3.07×10^{-5} mol/ml of I_2 with a corresponding specific activity of 47,375,000 cpm ml^{-1}

Kinetic Experiments. All kinetic runs were performed at 25 ± 0.5°. The reactions were initiated by ordinary fluorescent lighting of the laboratory. Individual kinetic runs were started by mixing a known volume of tagged iodine in CCl_4 with a known volume of the alkene in CCl_4. The length of the light path through the solutions was <1 cm. Variation of alkene concentration was accomplished by dilution of the alkene with CCl_4. After mixing, approximately 10-μl aliquots were withdrawn at regular intervals. In several duplicate runs where 100-μl aliquots were withdrawn, the results did not differ with those of 10 μl. The aliquots were extracted with equal volumes (5 ml) of aqueous sodium sulfite (which removed the inorganic iodine) and $CHCl_3$ (which removed the organically bound iodine). The $CHCl_3$ solution was dried over $CaCl_2$ and then 3.0-ml aliquots of the Na_2SO_3 extract and of the $CHCl_3$ extract were taken for assay. The activity of each solution was measured by counting the ^{131}I in a 2 in. × 2 in. NaI(Tl) well crystal. The ratio of activity of the organic phase to the total activity of both phases represented the fraction of the original iodine that had added to the double bond. The reaction was followed until no further addition of iodine could be detected. In several instances the reaction mixture was allowed to stand for several days to ensure completion of the reaction.

Product Separation and Identification. The products were identified by nmr spectroscopy. The observed spectra of 1-pentene and the corresponding 1,2-diiodopentane agreed well with those reported by Sumrell, *et al.*[2] The identification of the spectra of the *dl*- and *meso*-2,3-diiodopentanes produced by the addition of iodine to *trans*- and *cis*-2-pentene, respectively, was made on the basis of comparison with the known spectra of the *dl*- and *meso*-2,3-dichloro- and 2,3-dibromopentanes. The products from 2-methyl-2-butene were not investigated.

The pure vicinal diiodides could be obtained in the following manner. To 25 ml of the crude product (1,2-diodide, *meso*- and *dl*-2,3-diiodopentanes) was added 25 ml of CCl_4. The solution was extracted with aqueous Na_2SO_3 solution until no further decrease in color could be observed. The final solution was yellow-brown in color. The solution was dried over silica gel and distilled. The products were collected in greater than 80% yields at temperatures in the range of 90–135°. As the temperature of the pot was increased, decomposition of the distillation residue started to occur. The purified diiodides were reasonably stable at room temperature in the dark.

Conversion of Diiodides to Olefins. The conversion was accomplished by dehalogenation with zinc dust in methanol, or with magnesium turnings in ether. The latter method was more satisfactory. After the removal of the inorganic material, the hydrocarbon products were separated by distillation or by preparative gas phase chromatography. The product olefins were compared with the starting olefins by nmr spectroscopy.

Results

The addition of iodine to the double bond, in the various C_5 olefins studied, proceeds smoothly when the reaction is exposed to ambient light at 25°. Several kinetic runs were made in which the concentration of iodine was varied and the initial velocity of the reaction, as a function of iodine concentration, was determined. A double logarithmic plot of the velocity *vs.* the concentration of the added I_2 yielded a straight line, the slope being equal to the order of the reaction with respect to iodine. The reaction was found to be $^3/_2$ order with respect to iodine.

Since all kinetic runs were made with the respective alkene in excess, the rate of disappearance of iodine with respect to the concentration of iodine at time *t* can be expressed by

$$-d(I_2)_t/dt = k(I_2)^{3/2} \tag{1}$$

Integration of eq 1 yields the following expression

$$kt = 1/(a_0 - x) - (1/a_0) \tag{2}$$

where a_0 is the initial concentration of iodine at zero time, $(a_0 - x)$ the concentration of iodine at time *t*, and *t* the time in minutes. It is assumed that $(I) \propto (I_2)^{1/2}$, used in this and the following rate expressions, is valid for the low iodine concentrations and short light path employed in this study. Rate constants, *k*, were determined from the slopes of the straight lines obtained by plotting the values of $1/(a_0 - x)$ *vs.* *t*. A plot of the data for a representative run of each of the

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(8) S. W. Benson, D. M. Golden, and K. W. Egger, *J. Chem. Phys.*, **42**, 4265 (1965).

(9) R. L. Burwell, Jr., and R. G. Pearson, *J. Phys. Chem.*, **70**, 300 (1966).

(10) R. M. Noyes, D. E. Applequist, S. W. Benson, D. M. Golden, and P. S. Skell, *J. Chem. Phys.*, **46**, 1221 (1967).

(11) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Amer. Chem. Soc.*, **85**, 2859 (1963).

(12) P. S. Skell and P. O. Readio, *ibid.*, **86**, 3334 (1964).

C_5 alkenes is shown in Figure 1. Deviation of the reaction rates from eq 2 did not become serious until the reactions had proceeded to 75% completion or greater.

Within a few hours after the start of a reaction an equilibrium was established. At that point the reaction was 75–99% complete, depending on the original concentrations of the reactants and the nature of the alkene. This observed equilibrium could result from either or both of the following: (1) a true equilibrium established by the previously demonstrated[13] iodine atom catalyzed decomposition of the products, and/or (2) competition for the unreacted iodine *via* the formation of a charge-transfer complex of iodine with the product, the effect being a decrease in the concentration of uncombined iodine. The well-established photoaccelerated decomposition of various vicinal diiodides[14–16] would suggest that the decomposition of the product predominantly accounts for the observed equilibrium.

Although the reactions became complex in their later stages, the kinetics could be studied readily up to at least 75% completion, as demonstrated by the data in Figure 1.

The reaction between labeled iodine and 1-pentene was studied as a function of the initial concentrations of both iodine and 1-pentene. The results are given in Table I. The $^3/_2$ dependence of the reaction rate on the iodine concentration is demonstrated by the results of runs 1–5.

Table I. Rate Constants for the Addition of Iodine to 1-Pentene in Carbon Tetrachloride at 25°

Run	(I_2), mol/l. × 10^3	(1-Pentene), mol/l.	k, min^{-1} mol$^{-1/2}$ l.$^{1/2}$ × 10^2	(1-Pentene)/k, min mol$^{3/2}$ l.$^{-3/2}$
1	21.89	9.12	10.9	83.26
2	8.83	9.13	10.9	83.26
3	0.076	9.11	11.5	79.2
4	0.152	9.10	12.1	75.2
5	0.147	8.78	11.2	78.4
6	1.18	7.02	9.7	72.6
7	1.18	5.27	8.0	65.8
8	1.18	3.51	6.4	64.8
9	1.18	1.76	4.01	44.1

If the reaction was first order in 1-pentene concentration, the values of (1-pentene)/k would be independent of 1-pentene concentration. The last column of Table I, runs 5–9, indicates that this is not so. As the concentration of 1-pentene was decreased, there was also a marked decrease in the ratio. This suggests that the order with respect to 1-pentene is more complex. A more complex order would be expected if a 1-pentene–iodine charge-transfer complex was involved in the rate-limiting step of the reaction (*vide infra*).

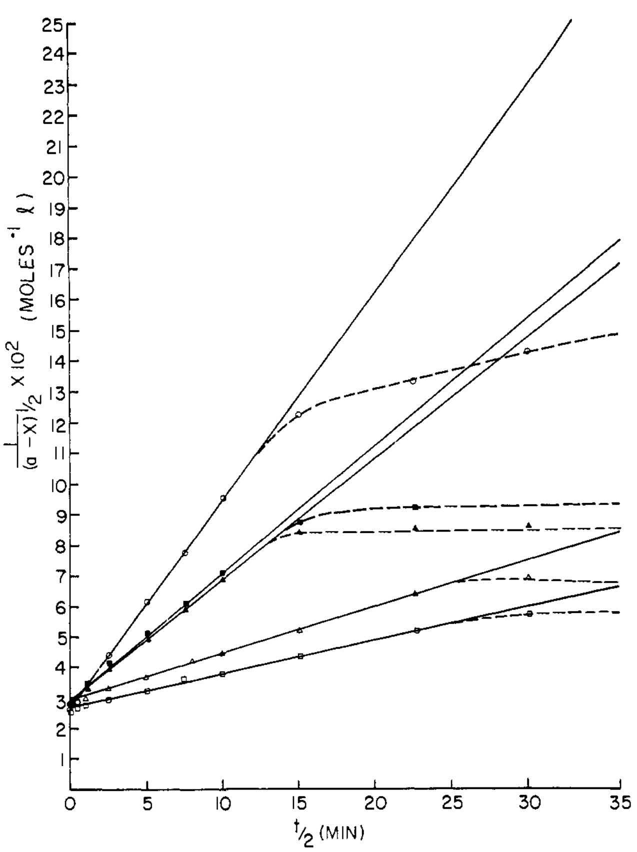

Figure 1. Rate curves for the addition of iodine to olefins, as a function of time: 1-pentene, ○; *cis*-2-pentene, ■; 2-methyl-1-butene, ▲; 2-methyl-2-butene, △; and *trans*-2-pentene, □.

Additional evidence suggesting the importance of the iodine–olefin charge-transfer complex, with respect to the addition of iodine to the double bond, was obtained by comparison of the reaction rates of a series of C_5 alkenes with their relative equilibrium constants for complex formation with iodine. Table II lists the rate constants obtained in this study, along with the relative equilibrium constants obtained by Cvetanović and coworkers.[17] It can be seen from the table that there is a rough correlation between the rate of the reaction and the ability of the olefin to act as a donor toward iodine. Because of the complexity of the kinetic relationships, one would not expect an exact correlation. It is gratifying, however, that an overall trend in the anticipated direction is observed. This is precisely

Table II. Comparison of Rate Constants of Iodination with the Relative Equilibrium Constants of Charge-Transfer Complexes

Olefin	k,[a] min mol$^{1/2}$ l.$^{1/2}$ × 10^2	Relative K_c[b]
1-Pentene	11.0	12.7
cis-2-Pentene	7.04	4.0
2-Methyl-1-butene	6.74	0.80
trans-2-Pentene	1.03	0.56

[a] Obtained with initial concentration of iodine of 1.8 × 10^{-3} mol/l. in neat pentenes. [b] Obtained from ref 17. The values are relative to *cis*-2-butene, which was taken as unity. It should be pointed out that Cvetanović, *et al.*, gave several values to choose from. The values quoted here are possibly the best values although the other choices showed the same general trend. *Cf.* W. E. Falconer and R. J. Cvetanović, *J. Chromat.*, **27**, 20 (1967).

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[17] R. J. Cvetanović, D. J. Duncan, W. E. Falconer, and W. A. Sunder, *ibid.*, **88**, 1602 (1966).

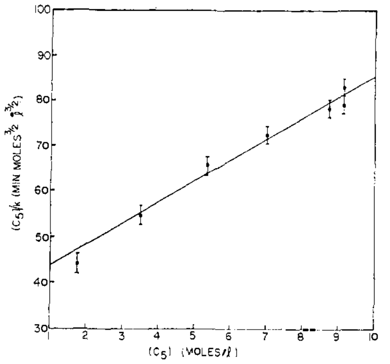

Figure 2. Plot used in the determination of K_c and k_1, according to eq 7.

what would be expected if the iodine–olefin charge-transfer complex was involved in the rate-determining step.

However, as noted by Furuyama, Golden, and Benson,[18] I atoms would also be expected to form complexes with the alkene bond. Although we are unaware of any data on the relative equilibrium constants of I–olefin charge transfer complexes for the various pentene isomers of interest, we might expect their relative values to follow the same general trend as the corresponding molecular iodine complexes. If this is true, the argument for the importance of the iodine–olefin charge-transfer complex would be equally applicable to the iodine atom complexes with the various pentene isomers.

The effects of alkene concentration and complexing ability on the observed k values can be explained by eq 3–10 in which eq 7 and/or 8 are rate determining

$$I_2 + h\nu \xrightarrow{i} 2I\cdot \qquad (3)$$

$$I_2 + C_5 \overset{K_c}{\rightleftharpoons} C_5\cdot I_2 \qquad (4)$$

$$I\cdot + C_5 \overset{K_c'}{\rightleftharpoons} C_5\cdot I \qquad (5)$$

$$C_5\cdot I_2 + h\nu \xrightarrow{i} C_5\cdot I + I\cdot \qquad (6)$$

$$C_5\cdot I_2 + I \xrightarrow{k_1} C_5I_2 + I\cdot \qquad (7)$$

$$C_5\cdot I + I_2 \xrightarrow{k_1'} C_5I_2 + I\cdot \qquad (8)$$

$$I\cdot + I\cdot \xrightarrow{t} I_2 \qquad (9)$$

$$I\cdot + C_5I \xrightarrow{t} C_5 + I_2 \qquad (10)$$

where i and t refer to the initiation and termination steps, respectively.

Before determining the rate law or laws required by the above reaction scheme, several factors need to be considered: (1) the I_2–olefin complex absorbs as well, if not better, than the free iodine. Therefore, eq 6 would be expected to contribute at least as much to the iodine atom formation as does eq 3. (2) Iodine atoms probably form π complexes with olefins just as strongly as does molecular iodine. Thus, the formation of the diiodide products by either eq 7 or 8 is possible. (3) Both eq 7 and 8 lead to the same transition state. Therefore, the kinetic data should not be expected to distinguish between them.

Assuming eq 7 to be rate determining, and the I_2–olefin complex to contribute equally to the iodine atom formation (eq 6), then, as shown in the Appendix, this mechanism would require a rate law of the form

$$d(C_5I_2)/dt = k_1K_c(I_2)^{3/2}(C_5)/(1 + K_c(C_5)) \qquad (11)$$

where K_c is the equilibrium constant for complex formation as defined by

$$K_c = (C_5I_2)/(C_5)(I_2) \qquad (12)$$

As shown in the Appendix, the observed rate constant k should then be related to k_1 by the expression

$$(C_5)/k = 1/(k_1K_c) + (C_5)/(k_1) \qquad (13)$$

According to eq 13, a plot of the experimental values of $(C_5)/k$ *vs.* (C_5) should yield a straight line, the slope and intercept of which should yield the values of k_1 and K_c, respectively. The data of Table I were treated graphically according to eq 13. From the resultant plot (Figure 2), values of $K = 1.0 \times 10^{-1}$ mol^{-1} l. and $k_1 = 2.38 \times 10^{-1}$ min^{-1} mol$^{-1/2}$ l.$^{1/2}$ were obtained.

Alternatively, if eq 8 is considered to be the rate-determining step, the required rate law is

$$d(C_5I_2)/dt = k_1'K_c'(I_2)^{3/2}(C_5)/(1 + K_c(C_5)) \qquad (14)$$

where K_c' is the equilibrium constant for the iodine atom–olefin complex formation as defined by

$$K_c' = (C_5I)/(C_5)(I) \qquad (15)$$

The rate expression for eq 8 is the same as that previously obtained for eq 7, with the exception of K_c' in the numerator. The slope and intercept of a plot of $(C_5)/k$ *vs.* (C_5) would be equal to $K_c/(k_1'K_c')$ and $1/(k_1'K_c')$, respectively. Accordingly, the value of k_1' is dependent on the value of K_c', but the value of K_c can be obtained from either rate expression. If $K_c' = K_c$, the rate constants k_1 and k_1' would be equal.

Andrews and Keefer[19] reported that the absolute value of the equilibrium constant for the cyclohexene–iodine complex was 0.34 mol^{-1} l. Cvetanović, *et al.*,[17] gave a relative value for cyclohexene. Combining these data with the relative equilibrium constant for 1-pentene allows the calculation of the absolute value for 1-pentene. This comes out to be 9.0×10^{-2} mol^{-1} l. This compares very favorably with the independent value obtained in this study. If we had neglected the contribution of iodine atoms from eq 6 the value for K_c, obtained from our kinetic data, would have been 7.07×10^{-2} mol^{-1} l. which compares less favorably with the 9.0×10^{-2} mol^{-1} l. value. This would seem to support the importance of eq 6 in the overall production of iodine atoms; however, the data are not precise enough to use this number to distinguish between the two possible mechanisms.

Identification of the products of the addition of iodine to 1-pentene and *cis*- and *trans*-2-pentene was made on the basis of their characteristic nmr spectra.[20] The nmr spectra of the respective starting olefins were identical with the products of elimination of iodine from

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(19) L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 74, 458 (1952).

(20) The nmr data in ref 1 were used to identify 1,2-diiodopentane. The *meso*- and *d,l*-2,3-diiodopentanes were identified on the basis of comparison of their nmr spectra with the spectra of the chloro and bromo analogs found in Stadtler NMR Spectra, Stadtler Research Laboratories, Philadelphia, Pa.

the corresponding diiodides. The 1,2-diiodopentane was readily converted to 1-pentene by stirring with zinc dust in methanol. Similar treatment of the *dl*- and *meso*-2,3-diiodopentanes, however, produced considerable quantities of pentane. The iodine-catalyzed conversion of an alkene to its corresponding alkane has been reported previously.[21] However, conversion of the 2,3-diiodopentanes back to their respective *cis*- and *trans*-2-pentenes was successfully accomplished by stirring with magnesium in ethyl ether. Although pentane was also produced in this reaction, it was in a much smaller amount, and sufficient quantities of the *cis*- and *trans*-2-pentenes were recovered to confirm the reported[3] stereospecific nature of the addition and elimination of iodine.

Attempts to convert the respective diiodo products back to their starting materials by thermal decomposition were unsuccessful. When 1,2-diiodopentane and the 2,3-diiodopentanes were heated without prior removal of the small quantities of excess iodine, decomposition occurred at *ca.* 35°, resulting in the formation of HI and a dark polymeric material of unknown composition. However, if the excess iodine were removed prior to heating by an aqueous sulfite extraction, the respective diiodides could be distilled at *ca.* 130°, with little accompanying thermal decomposition.

Discussion

Assuming a mechanism based on either eq 7 or 8 we were able to obtain reproducible experimental values for the rate constant, consistent with the rate law for that mechanism. In addition, the expected correlation between reaction rates and complexing ability of the respective olefins was found. The value obtained for the charge-transfer equilibrium constant for the 1-pentene–iodine complex was consistent with the reported value for the iodine–cyclohexane complex.[19] It would therefore appear that, assuming similar complexing of the olefins with iodine atoms, either postulated mechanism is sufficiently justified by our experimental data. Since both eq 7 and 8 require activated complexes having identical configurations, our kinetic measurements would not be expected to distinguish between the alternate mechanisms.

Our mechanism, assuming eq 7 to be the rate-determining step, is also in complete agreement with other studies which suggested that a concerted addition mechanism was required for the addition of iodine to alkenes. Most of these studies dealt with the reverse of the addition reaction[14,15] and with isomerization of olefins by iodine.[8,10] Agreement with the reported[3] stereospecific nature of the iodine addition and elimination is also consistent with our proposed mechanism, since the π complex would be expected to collapse stereospecifically. Although our observations can be explained without assuming the existence of a bridged radical intermediate, we can offer no definitive evidence to either prove or disprove the importance of the $C_5 \cdot I$ radical in the formation of the observed diiodo products. However, if the iodine atom reacts with the olefin first, in the sequence leading to final products, the stereospecific nature of the iodine addition–elimination requires a bridged radical structure, as proposed by Skell, *et al.*,[3] for the C_5I intermediate.

The observed deviation of the experimental values from the straight line plots in Figure 1, which occur in the later stages of the reaction, and the subsequent attainment of an equilibrium, suggest that the proposed mechanisms and the resultant kinetic expressions do not fully describe the iodine interaction with the alkene. In fact, eq 7 would be more correctly expressed as

$$C_5I_2 + I \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_5I_2 + I \tag{16}$$

allowing for the reversible decomposition of the products.

A series of five solutions, containing varying concentrations of iodine between 1.0×10^{-2} and 1.0×10^{-3} mol l.$^{-1}$ in neat 1-pentene, were allowed to stand for 48 hr, and the equilibrium concentrations of the respective reactants and products were determined. The expression for the overall equilibrium constant for eq 7, assuming the reaction was reversible, would be

$$K = (C_5I_2)/(C_5 \cdot I_2) \tag{17}$$

and from eq 12 $(C_5 \cdot I_2)$ is equal to $K_c(C_5)(I_2)$. The expression for the observed equilibrium constant, K_{obsd}, would then be

$$K_{obsd} = KK_c = (C_5I_2)/(C_5)(I_2) \tag{18}$$

Using eq 18, the average value of the observed equilibrium constant, K_{obsd}, was found to be 2.51 ± 0.20. Using this value and the value determined previously for K_c, the value of K was found to be 25.10.

The kinetic expression should include an additional term allowing for the reversible step. Polissar[14] and others[11,12] have shown that the decomposition of vicinal diiodides proceeds by an I-atom-catalyzed concerted process, *i.e.*, essentially the reverse of our addition mechanism. Thus, eq 12 could be rewritten to give

$$\begin{aligned} d(C_5I_2)/dt = k_1K_c(I_2)^{3/2}(C_5)/(1 + K_c(C_5)) - \\ k_2(C_5I_2)(I_2)^{1/2} \end{aligned} \tag{19}$$

which includes the expression for the product decomposition. By the inclusion of the decomposition term in the overall kinetic expression, our observed data should cover the entire range of the reaction. However, this is not necessary in order to ascertain the composition of the transition state. As demonstrated by our data, the decomposition term may be neglected, and sufficient data can be obtained from the initial stages of the reaction to identify the empirical formula of the transition state.

As discussed previously, the diiodo products were converted back to their respective olefins, and the stereospecific nature of the addition–elimination cycle of iodine was confirmed. The dependence of the thermal stability of the products on the presence of iodine and the conversion of the pentenes to their respective pentanes, while interesting, were not pursued further.

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(21) K. W. Egger and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 236 (1966).

Appendix

The initial rate equation was derived assuming the following

$$I_2 + h\nu \xrightarrow{\text{i}} 2I \qquad (1A)$$

$$I_2 + C_5 \overset{K_c}{\rightleftharpoons} C_5 \cdot I_2 \qquad (2A)$$

$$C_5 \cdot I_2 + h\nu \longrightarrow C_5 \cdot I + I\cdot \qquad (3A)$$

$$C_5 \cdot I_2 + I\cdot \xrightarrow{k_1} C_5I_2 + I\cdot \qquad (4A)$$

$$I + I \xrightarrow{\text{t}} I_2 \qquad (5A)$$

$$C_5 \cdot I + I \xrightarrow{\text{t}} C_5 + I_2 \qquad (6A)$$

For the purpose of this derivation, it was assumed that eq 4A was rate determining and irreversible. In addition, eq 3A was assumed to contribute to the production of iodine atoms in a manner similar to eq 1A.

The rate of formation of product according to eq 4A is given by

$$d[C_5I_2]/dt = k_1[C_5 \cdot I_2][I_2]_{\text{eff}}^{1/2} \qquad (7A)$$

where $[I_2]_{\text{eff}}$ is the effective iodine concentration leading to the production of iodine atoms, which includes the contribution from eq 3A, as expressed by

$$[I_2]_{\text{eff}} = [I_2]_f + [C_5 \cdot I_2] \qquad (8A)$$

and

$$[I_2]_f = \text{concentration of uncomplexed iodine} = [I_2] - [C_5 \cdot I_2] \qquad (9A)$$

thus

$$[I_2]_{\text{eff}} = [I_2] \qquad (10A)$$

The charge-transfer equilibrium constant is defined by

$$K_c = \frac{[C_5 \cdot I_2]}{[C_5][I_2]_f} \qquad (11A)$$

Substituting the expression for $[I_2]_f$ into eq 11A and rearranging, we obtain the expression for the concentration of the complex

$$[C_5 \cdot I_2] = \frac{K_c[C_5][I_2]}{1 + K_c[C_5]} \qquad (12A)$$

Substitution of eq 12A into eq 7A and rearrangement give

$$[I_2]^{-3/2}d[C_5I_2]/dt = \frac{k_1K_c[C_5]}{1 + K_c[C_5]} \qquad (13A)$$

Since the observed rate constant is given by eq 14A

$$d[C_5I_2]/dt = k[I_2]^{3/2} \qquad (14A)$$

it can be rewritten in terms of eq 13A to give eq 15A.[22]

$$\frac{[C_5]}{k} = \frac{1}{k_1K_c} + \frac{[C_5]}{k_1} \qquad (15A)$$

According to eq 15A a plot of $[C_5]/k$ *vs.* $[C_5]$ would give a straight line whose slope would be equal to $1/k_1$ and the intercept equal K_c/k_1.

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[22] This rate expression is similar to the one arrived at by Keefer and Andrews in a study of the exchange reactions between organic halides and iodine monochloride. *Cf.* R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **75**, 543 (1953); **76**, 253 (1954).

Kinetics of Dye Formation by Flash Photolysis. In 1-Octanol

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Abstract: Azomethine dye is formed when *p*-azido-*N,N*-diethylaniline is photolyzed in the presence of 2,6-dimethylphenol derivatives in 1-octanol. Nitrene, formed in the photolysis, reacts at the position para to hydroxyl on the phenol to form a leuco dye or abstracts a proton to form quinonediimine. Leuco dye is converted to dye by elimination of a suitably positioned leaving group or by oxidation with quinonediimine. This rate-determining step (*i.e.*, conversion of leuco dye to dye) is accelerated by acidic materials and has only minor dependence on coupler ionization.

Azomethine dye is formed when quinonediimine reacts with a phenolic or naphtholic compound called a coupler. This reaction may occur in an aqueous phase or in a low dielectric organic solvent. The kinetics and mechanism of dye formation and the associated reactions of quinonediimine have been established for the aqueous phase.[1–4] The present work was undertaken to supply information regarding dye formation in organic solvents.

Tong and Glesmann[1] have shown that, in aqueous systems, quinonediimine reacts reversibly with coupler ion to form an intermediate called a leuco dye. Colorless leuco dye is converted to dye by formation of a double bond through an elimination reaction or an oxidation reaction. If a leaving group (X) other than hydrogen is para to hydroxyl on the phenolic or naphtholic coupler, the dye forms by elimination, and the coupler is referred to as "two-equivalent." When hydrogen is para to hydroxyl, the leuco dye must be oxi-

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[1] L. K. J. Tong and M. C. Glesmann, *J. Amer. Chem. Soc.*, **90**, 5164 (1968).

[2] L. K. J. Tong and M. C. Glesmann, *ibid.*, **79**, 583 (1957).

[3] L. K. J. Tong, *J. Phys. Chem.*, **58**, 1090 (1954).

[4] L. K. J. Tong, M. C. Glesmann, and R. L. Bent, *J. Amer. Chem. Soc.*, **82**, 1988 (1960).