Reactions of Allylic Radicals

Part 1.—Disproportionation between Allyl and Ethyl Radicals

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Allyl radicals may be generated in the presence of a large excess of ethyl radicals by the illumination of a gaseous mixture of diethyl ketone and diallyl with 3130 Å light between 134 and 175°C. Generation proceeds by the sequence of reactions:

$$C_2H_5^{\bullet}+C_6H_{10}\rightarrow C_8H_{15}^{\bullet}\rightarrow C_5H_{10}+C_3H_5^{\bullet}$$

having activation energies of 6·6±0·4 and 16±4 kcal/mole respectively. Conditions may be controlled so that the allyl radicals are removed exclusively by combination and disproportionation with ethyl radicals, and the allene and propene found among the products are formed solely by the two possible modes of this cross-disproportionation. Product analysis reveals the pattern of combination and disproportionation between allyl and ethyl radicals:

$$\begin{array}{lll} C_3H_5^{\bullet}+C_2H_5^{\bullet}\rightarrow C_5H_{10} & (85\pm4)\ \% & [90\ \%] \\ \qquad\qquad\quad\rightarrow C_3H_4+C_2H_6 & (4\pm1)\ \% & [3\ \%] \\ \qquad\qquad\quad\rightarrow C_3H_6+C_2H_4 & (11\pm3)\ \% & [7\ \%] \end{array}$$

The experimental results agree moderately well with the corresponding values calculated from the equation of Holroyd and Klein, and which are given above in square brackets. These results are discussed in relation to the patterns of disproportionation and combination found for the allyl radical in other systems.

The allyl radical is an important intermediate in the pyrolysis,[1-4] photolysis [5-8] and radiolysis [9] of several olefins and cycloalkanes, and of certain of their derivatives. Mass spectrometry has identified the allyl radical as a major product of the pyrolysis of allyl iodide, diallyl, butene-1[10] and cyclopentylmethyl nitrite,[11] and of the mercury-sensitized photolysis [12] of propene, butene-1 and isobutene. The electron spin resonance spectrum of the allyl radical has been observed in liquid cyclopropane irradiated with 2·8 MeV electrons,[13] in solid propene irradiated with γ-rays from a ^{60}Co source,[14] and in solid allyl bromide containing a small proportion of sodium.[15]

The allyl radical may be expected to show the reactions of addition, metathesis, combination and disproportionation characteristic of a hydrocarbon free radical. Evidence for such reactions has been sought in a wide variety of systems, but below 300°C the great majority of allyl radicals are commonly consumed by mutual or cross combination, and disproportionation accounts for the small remainder. Metathetical and addition reactions of the allyl radical are rendered kinetically negligible below 300°C [16, 17] by their high energies of activation.[18] For example, the energy of activation for metathesis with cyclopentane is 32 kcal/mole for the allyl radical but only 9·3 kcal/mole for the methyl radical.[19] The difference in these energies of activation arises mainly from the delocalization energy of the allyl radical, a significant quantity in this investigation.

Disproportionation between the allyl radical and an alkyl radical is often assumed to be kinetically negligible. This assumption seems to be based [9] upon the

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mass spectrometric study of the pyrolysis of allyl iodide at 750°C; [10] the results imply that when two allyl radicals interact, mutual combination is more than 100 times as probable as mutual disproportionation. There is a need for reliable quantitative information upon the reactions of cross-disproportionation between the allyl radical and a representative alkyl radical; the lack of such information imposes a serious limitation upon the interpretation of the kinetics of many pyrolytic, photolytic and radiolytic systems. The aim of this investigation is to assess quantitatively the extent and pattern of the disproportionation reactions of the allyl radical in a representative system under conditions which would allow an unambiguous interpretation of the results.

Allene and propene are the characteristic products of the two possible modes of disproportionation of the allyl radical, either with itself or with another alkyl radical. We have chosen to study the pattern of disproportionation of the allyl radical with the ethyl radical, as the latter is the simplest alkyl radical capable of both modes:

$$C_2H_5^{\cdot}+C_3H_5^{\cdot}\rightarrow C_2H_6+C_3H_4$$
$$\rightarrow C_2H_4+C_3H_6.$$

The method of generation of the allyl radical must conform to three conditions if the interpretation of the results is to be unambiguous. First, the source must yield allyl and ethyl radicals in abundance, and interfering radicals in negligible quantities only. Secondly, any propene or allene found among the products must have been formed from the allyl radicals exclusively by disproportionation. A reaction temperature below 300°C ensures that the allyl radical will not yield significant amounts of propene by metathesis [18] or of allene by loss of a hydrogen atom.[20] Mercury resonance radiation must not be used, as it may yield allene through the process [12]:

$$\text{Hg}\ {}^3P_1+C_3H_5^{\cdot}\rightarrow \text{Hg}\ {}^1S_0+C_3H_4+H^{\cdot}\ .$$

Thirdly, the ethyl radical must be formed in great excess over the allyl radical, to ensure that the only significant reactions of disproportionation of the allyl radical are those given above with the ethyl radical. Such conditions eliminate the known sources of the allyl radical, in particular, the two sources commonly used for kinetic studies: the thermal decomposition of the cyclopentyl radical [19] and of the diallyl molecule.[1, 2, 21] Under the conditions that yield allyl radicals the former is now known to give hydrogen atoms [11, 22] and the latter is suspected of undergoing a degenerate Cope rearrangement [23]; neither yields allyl radicals below 300°C.

Propene, cyclopropane and their derivatives are the natural starting materials for the preparation of the allyl radical, and photolysis and radiolysis are the obvious methods for generation below 200°C. The concomitant generation of other reactive species renders the radiolytic method unattractive.[9, 13, 24] Direct photolysis was considered for a number of promising substrates, but each possesses some serious disadvantage. Photolysis of dicyclopropyl ketone is likely to lead only to isomerization,[25] and photolysis of diallyl ketone should proceed largely by a type II process [26]; the corresponding aldehydes, cyclopropyl aldehyde [27] and 3-butenal,[28] were even less suitable as sources. Propene,[5] butene-1 [5] and cyclopropane [6] each yield allyl radicals in a primary photochemical process, but competing primary processes render them unattractive as sources. The photolysis of 3,3′-azopropene appears to be more promising, but no account of its synthesis could be found. Metathesis between the ethyl radical and propene demands the use of deuterated species if the pattern of disproportionation is to be fully investigated, and pentyl-2 radicals would be formed simultaneously by addition.[29, 30] Metathesis between the ethyl radical and cyclopropane is likely to be very slow in the desired range of temperature.[16]

A method for the generation of the allyl radical which fulfills all the required conditions has been found in the sequence of reactions:

$$CH_3CH_2\cdot + CH_2{=}CHCH_2CH_2CH = CH_2 \rightarrow$$

$$CH_3CH_2CH_2\dot{C}HCH_2CH_2CH = CH_2\,; \quad \Delta H = -22\ \text{kcal}$$

$$CH_3CH_2CH_2\dot{C}HCH_2CH_2CH = CH_2 \rightarrow$$

$$CH_3CH_2CH_2CH = CH_2 + [CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} CH_2]\cdot\,; \quad \Delta H = +11\ \text{kcal.}$$

The delocalization energy of the allyl radical reduces the enthalpy of the dismutation reaction sufficiently to yield the allyl radical at a suitable rate between 134 and 175°C.

Ethyl radicals were generated in the presence of diallyl by the illumination of a gaseous mixture of diethyl ketone and diallyl with 3130 Å radiation. Reaction conditions were controlled so that the ethyl radical was always present in great excess over the allyl radical, and no other radical formed in the system could interfere with the interpretation of the results.

EXPERIMENTAL

PROCEDURE

The apparatus and general method have been described previously.[31] The reagents were of the purest grade obtainable commercially; each was further purified by gas chromatography and the purity of the selected fraction established using the 2m column R of the Perkin Elmer Vapour Fractometer, model 154C.

The major products were: CO, C_2H_4, C_2H_6, C_4H_{10} and pentene-1, and by inference, diallyl, which was indistinguishable from the reactant. Numerous minor products were formed at rates which increased rapidly with temperature; those of kinetic interest were identified and estimated, and included: C_2H_2, C_3H_4, C_3H_6, butene-1, butadiene-1,3, cyclohexadiene-1,3 and two other C_6H_8 isomers.

The products were separated into four fractions by a Ward-LeRoy still operating successively at −210, −150, −120 and +25°C; the amount of each of the first three fractions was estimated by a gas burette. The mass spectrometer showed that the −210° fraction was pure CO. The other three fractions were analyzed by the Vapour Fractometer using a flame ionization detector. The −150° fraction was separated into its components by the 2m silica gel column J at 85°; the components were eluted in the order: C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_4, and their rates of formation were determined from the corresponding areas of the chromatogram using an appropriate standardization procedure. The −120° fraction comprised some or all of the components: n-butane, butene-1, butadiene-1,3, pentene-1, and some of the reactant diallyl. A known proportion of this fraction was analyzed for C_4H_{10}, C_4H_8, C_4H_6, C_5H_{10} and C_6H_{10} using the 2m silica gel column at 160°. The remainder was combined with the 25° fraction and the whole separated into its constituents by the polyethylene glycol column R at 60°. Peaks were found for an unresolved C_4 fraction, pentene-1, diallyl, two C_6H_8 isomers, cyclohexadiene-1,3, and diethyl ketone. The rate of formation of each of the C_4, C_5 and C_6 products, except diallyl, was estimated from the two appropriate chromatograms. The two C_6H_8 isomers were tentatively identified as the cis and trans isomers of hexatriene-1,3,5. Cyclohexadiene-1,4 and benzene could have been detected in trace amounts as they would have given well-separated peaks between those for cyclohexadiene-1,3 and diethyl ketone; they were sought, but never found among the products.

A principal aim of this investigation is to measure the extent of disproportionation between the allyl and ethyl radicals, and we must establish that allene and propene, the products of this disproportionation, were not consumed by interaction with ethyl radicals in our systems. The stability of the product butadiene-1,3 is also of interest. Accordingly we have performed a control experiment in which diethyl ketone was photolyzed at 172°C in the presence of allene, propene and butadiene, each in amounts representative of the final composition of a normal experiment at that temperature, and the system was analyzed before and after illumination at normal intensity for 7200 sec. The initial composition was: diethyl ketone, 187 μmole; allene, propene and butadiene: 23·8, 94·2 and 47·6 mμmole respectively. The final composition was: allene, propene and butadiene: 23·2, 93·0 and 47·0 mμmole respectively. The recovery of the hydrocarbons was therefore about 98 % under typical conditions at the high-temperature region of this study; such a result allows us to pursue the kinetic analysis with confidence.

KINETIC ANALYSIS

Under the experimental conditions of this investigation the photolysis of diethyl ketone conforms to the simple mechanism [32]:

$$CH_3CH_2COCH_2CH_3 + h\nu \rightarrow 2CH_3CH_2^{\bullet} + CO \tag{1}$$

$$2CH_3CH_2^{\bullet} \rightarrow CH_3CH_2CH_2CH_3 \tag{2}$$

$$\rightarrow CH_3CH_3 + CH_2{=}CH_2 \tag{3}$$

$$CH_3CH_2^{\bullet} + CH_3CH_2COCH_2CH_3 \rightarrow CH_3CH_3 + CH_3\dot{C}HCOCH_2CH_3 \tag{4}$$

$$CH_3CH_2^{\bullet} + CH_3\dot{C}HCOCH_2CH_3 \rightarrow CH_3CH(CH_2CH_3)COCH_2CH_3. \tag{5}$$

If a gaseous mixture of diethyl ketone and diallyl is illuminated the ethyl radicals also react with diallyl, and both addition and metathesis are observed. No extra products are found in the C_1–C_4 range for reaction temperatures below 134°C, and the mechanism is adequately supplemented by the reactions:

$$CH_3CH_2^{\bullet} + CH_2{=}CHCH_2CH_2CH{=}CH_2 \rightarrow$$
$$CH_3CH_3 + [CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} CH.CH_2CH{=}CH_2]^{\bullet} \tag{6}$$

$$CH_3CH_2^{\bullet} + [CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} CH\,.\,CH_2CH{=}CH_2]^{\bullet} \rightarrow$$
$$CH_2{=}CHCH(CH_2CH_3)CH_2CH{=}CH_2 \tag{6c'}$$
$$\rightarrow CH_3CH_2CH_2CH{=}CH{\cdot}CH_2CH{=}CH_2 \tag{6c''}$$
$$\rightarrow CH_3CH_3 + CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2 \tag{6d}$$

(cis and trans isomers)

$$\text{cis-}CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2 \rightarrow \text{cyclohexadiene-1,3} \tag{6i}$$

$$CH_3CH_2^{\bullet} + CH_2{=}CHCH_2CH_2CH{=}CH_2 \rightarrow$$
$$CH_3CH_2CH_2CHCH_2CH_2CH{=}CH_2 \tag{7}$$

$$CH_3CH_2^{\bullet} + CH_3CH_2CH_2\dot{C}HCH_2CH_2CH{=}CH_2 \rightarrow$$
$$CH_3CH_2CH_2CH(CH_2CH_3)CH_2CH_2CH{=}CH_2 \tag{7c}$$

Reactions (6*d* and (6*i*) were included to account for the formation in trace amounts of two C_6H_8 isomers at 91°C, and of the same two isomers and cyclohexadiene-1,3 at 164°C. Cyclohexadiene-1,4 was not present among the products at either temperature, and the two C_6H_8 isomers were tentatively identified as the cis and trans forms of hexatriene-1,3,5. Hexatriene-1,cis-3,5 is known to isomerize readily to cyclohexadiene-1,3 by both thermal [33] and photochemical [34] processes. The ratio of the amount of the trans isomer to the sum of the amounts of the cis isomer and cyclohexadiene-1,3 was 0·37 at 91°C and 0·33 at 164°C, suggesting that the cis and trans isomers are the initial products of disproportionation, and that some of this cis isomer isomerizes to cyclohexadiene-1,3 at the higher temperature.

At 134°C appreciable quantities of pentene-1 begin to appear among the products, accompanied by much smaller amounts of allene and propene. Such products are consistent with the dismutation of the adduct radical formed in reaction (7) to yield the allyl radical and pentene-1; the allyl radical would be consumed exclusively by interaction with the ethyl radical, since the latter is present in great excess:

$$CH_3CH_2CH_2\dot{C}HCH_2CH_2CH{=}CH_2 \rightarrow$$
$$CH_3CH_2CH_2CH{=}CH_2 + [CH_2 \dashrightarrow CH \dashrightarrow CH_2]\cdot \qquad (8)$$
$$CH_3CH_2^{\bullet} + [CH_2 \dashrightarrow CH \dashrightarrow CH_2]\cdot \rightarrow CH_3CH_2CH_2CH{=}CH_2 \qquad (8c)$$
$$\rightarrow CH_3CH_3 + CH_2{=}C{=}CH_2 \qquad (8d)$$
$$\rightarrow CH_2{=}CH_2 + CH_3CH{=}CH_2\cdot \qquad (8e)$$

At 154°C small amounts of butadiene-1,3 and butene-1 and traces of acetylene begin to appear. These products are not formed in any other reaction in this system, and are consistent with the dismutation of the α-allyl allyl radical formed in reaction (6):

$$[CH_2 \dashrightarrow CH \dashrightarrow CH\,.\,CH_2CH{=}CH_2]\cdot \rightarrow CH_2{=}CH\,.\,CH{=}CH_2 + \cdot CH{=}CH_2 \qquad (9)$$

The vinyl radical should be consumed exclusively by interaction with the ethyl radical:

$$CH_3CH_2^{\bullet} + \cdot CH{=}CH_2 \rightarrow CH_3CH_2CH{=}CH_2 \qquad (9c)$$
$$\rightarrow CH_3CH_3 + CH{\equiv}CH \qquad (9d)$$
$$\rightarrow 2CH_2{=}CH_2 \qquad (9e)$$

This mechanism is supported by a material balance among the products of the reactions involving the vinyl radical. Five experiments performed between 161 and 175°C yielded the ratio

$$(C_4H_8 + C_2H_2)/C_4H_6 = 0{\cdot}97 \pm 0{\cdot}01.$$

The ethylene formed by reaction (9*e*) cannot be estimated directly, and the defect from unity of 0·03±0·01 in this ratio most probably arises from the neglect of this ethylene in the ratio. Indeed, a defect of 0·04 is predicted by the equation of Holroyd and Klein.[35]

Mutual interaction of allyl radicals is unlikely to occur to a significant extent under the reaction conditions of this investigation for reasons given below. We conclude that the mechanism is adequately represented by the reactions (1)-(9*e*) given above, and the rate constants are calculated on this basis.

To calculate the rates of metathesis, R_6, and addition, R_7, we must consider the total rates of formation of ethylene and ethane:

$$R_{C_2H_4} = R_3 + R_{8e} + 2R_{9e} = R_3 + R_{C_3H_6} + 0{\cdot}06R_{C_4H_6},$$
$$R_{C_2H_6} = R_3 + R_4 + R_6 + R_{6d} + R_{8d} + R_{9d}$$
$$= R_{C_2H_4} - R_{C_3H_6} - 0{\cdot}06R_{C_4H_6} + R_4 + R_6 + R_{C_6H_8} + R_{C_3H_4} + R_{C_2H_2}\,.$$
$$\therefore R_6 = [R_{C_2H_6} + R_{C_3H_6} + 0{\cdot}06R_{C_4H_6}] - [R_{C_2H_4} + R_{C_2H_2} + R_{C_3H_4} + R_{C_6H_8}] - (k_4/k_2^{\frac{1}{2}})[\mathrm{D}](R_{C_4H_{10}})^{\frac{1}{2}},$$

and

$$\frac{k_6}{k_2^{\frac{1}{2}}} = \frac{[R_{C_2H_6} + R_{C_3H_6} + 0{\cdot}06R_{C_4H_6}] - [R_{C_2H_4} + R_{C_2H_2} + R_{C_3H_4} + R_{C_6H_8}]}{[B](R_{C_4H_{10}})^{\frac{1}{2}}} - \frac{[\mathrm{D}]}{[B]}\frac{k_4}{k_2^{\frac{1}{2}}}.$$

The symbols [D] and [B] signify the concentration of diethyl ketone and diallyl respectively, and R_X represents the rate of formation of product X. The term $0{\cdot}06R_{C_4H_6}$ represents the ethylene formed by reaction (9*e*). Also,

$$R_7 = [R_{CO}+R_{C_2H_2}+R_{C_3H_4}+R_{C_6H_8}]-[R_{C_2H_6}+R_{C_4H_{10}}]$$

and

$$\frac{k_7}{k_2^{\frac{1}{2}}} = \frac{[R_{CO}+R_{C_2H_2}+R_{C_3H_4}+R_{C_6H_8}]-[R_{C_2H_6}+R_{C_4H_{10}}]}{[B](R_{C_4H_{10}})^{\frac{1}{2}}}.$$

The rate R_8 of the dismutation reaction may be obtained from the relationships:

$$2R_8 = R_8+R_{8c}+R_{8d}+R_{8e} = R_{C_5H_{10}}+R_{C_3H_4}+R_{C_3H_6},$$

$$\frac{R_8}{R_{7c}} = \frac{[R_{C_5H_{10}}+R_{C_3H_4}+R_{C_3H_6}]}{2(R_7-R_8)} = \frac{k_8k_2^{\frac{1}{2}}}{k_{7c}(R_{C_4H_{10}})^{\frac{1}{2}}},$$

$$\frac{k_8k_2^{\frac{1}{2}}}{k_{7c}} = \frac{[R_{C_5H_{10}}+R_{C_3H_4}+R_{C_3H_6}](R_{C_4H_{10}})^{\frac{1}{2}}}{[2(R_{CO}+R_{C_2H_2}+R_{C_6H_8})+R_{C_3H_4}]-[2(R_{C_2H_6}+R_{C_4H_{10}})+R_{C_3H_6}+R_{C_5H_{10}}]}.$$

A rate expression for the dismutation reaction (9) may be obtained from the relationships:

$$\frac{R_9}{R_{6c}} = \frac{R_{C_4H_6}}{R_6-R_{C_6H_8}-R_{C_4H_6}} = \frac{k_9}{k_{6c}}\frac{k_2^{\frac{1}{2}}}{(R_{C_4H_{10}})^{\frac{1}{2}}},$$

$$\frac{k_9k_2^{\frac{1}{2}}}{k_{6c}} = \frac{R_{C_4H_6}(R_{C_4H_{10}})^{\frac{1}{2}}}{[R_{C_2H_6}+R_{C_3H_6}]-[R_{C_2H_4}+R_{C_2H_2}+R_{C_3H_4}+0{\cdot}94R_{C_4H_6}+2R_{C_6H_8}]-(k_4/k_2^{\frac{1}{2}})[D](R_{C_4H_{10}})^{\frac{1}{2}}}$$

The patterns of disproportionation for the allyl, vinyl and ethyl radicals may be obtained from the equations:

$$\frac{k_{8d}}{k_8} = \frac{2R_{C_3H_4}}{[R_{C_5H_{10}}+R_{C_3H_4}+R_{C_3H_6}]}; \quad \frac{k_{8e}}{k_8} = \frac{2R_{C_3H_6}}{[R_{C_5H_{10}}+R_{C_3H_4}+R_{C_3H_6}]};$$

$$\frac{k_{9d}}{k_9} = \frac{R_{C_2H_2}}{R_{C_4H_6}}; \quad \frac{k_{9e}}{k_9} = \frac{R_{C_4H_6}-R_{C_4H_8}-R_{C_2H_2}}{R_{C_4H_6}}$$

$$k_3/k_2 = [R_{C_2H_4}-R_{C_3H_6}-0{\cdot}06R_{C_4H_6}]/R_{C_4H_{10}}.$$

RESULTS AND DISCUSSION

Table 1 lists the results of eleven experiments on the photolysis of a gaseous mixture of diethyl ketone and diallyl by 3130 Å radiation between 71 and 175°C. The symbols [D] and [B] signify the concentration of diethyl ketone and diallyl respectively, and R_X represents the rate of formation of the product X. Rate constants were calculated from the corresponding equations of the previous section, and are given below with appropriate limits of error estimated at the 5 % probability level:

$$k_6/k_2^{\frac{1}{2}} = 10^{(-8{\cdot}5\pm0{\cdot}2)}\exp(-6{\cdot}3\pm0{\cdot}4)10^3/\boldsymbol{R}T \text{ cm}^{\frac{3}{2}} \text{ molecule}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}},$$

$$k_7/k_2^{\frac{1}{2}} = 10^{(-7{\cdot}9\pm0{\cdot}2)}\exp(-6{\cdot}6\pm0{\cdot}4)10^3/\boldsymbol{R}T \text{ cm}^{\frac{3}{2}} \text{ molecule}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}},$$

$$k_7/k_6 = 10^{(0{\cdot}7\pm0{\cdot}2)}\exp(-0{\cdot}4\pm0{\cdot}4)10^3/\boldsymbol{R}T; \quad 2{\cdot}8\pm0{\cdot}4 \text{ at } 100°\text{C},$$

$$k_8k_2^{\frac{1}{2}}/k_{7c} = 10^{(13{\cdot}6\pm2{\cdot}0)}\exp(-16{\cdot}4\pm4{\cdot}0)10^3/\boldsymbol{R}T \text{ molecule}^{\frac{1}{2}} \text{ cm}^{-\frac{3}{2}} \text{ sec}^{-\frac{1}{2}}.$$

TABLE 1: THE PHOTOLYSIS OF A GASEOUS MIXTURE OF DIETHYL KETONE AND DIALLYL

temp	time	10^{-17}[D]	10^{-17}[B]				$10^{-12}R_X$ (molecule/cm³ sec)																
(°C)	(sec)	(molecule/cm³)		CO	C_2H_4	C_2H_6	C_4H_{10}	C_5H_{10}	C_3H_4	C_3H_6	C_4H_6	C_4H_8	C_2H_2	M	$\frac{k_3}{k_2}$	$\frac{k_{8c}}{k_8}$	$\frac{k_{8d}}{k_8}$	$\frac{k_{8e}}{k_8}$	$\frac{10^{13}k_6}{k_2^{\frac{1}{2}}}$	$\frac{10^{13}k_7}{k_2^{\frac{1}{2}}}$	$\frac{k_7}{k_6}$	$\frac{10^{-5}k_8k^{\frac{1}{2}}}{k_{7c}}$	$\frac{10^{-16}k_8k_2}{k_7k_7}$
71	1800	4·91	4·73	13·0	1·36	2·40	9·46	0·000	0·000	0·000	n.a.	n.a.	0·000	0·912	0·144	—	—	—	3·30	7·9	2·39	—	—
91	1800	4·00	5·43	13·1	1·28	2·85	7·87	0·017	n.a.	n.a.	n.a.	n.a.	0·000	0·818	(0·163)	—	—	—	5·20	15·7	3·02	—	—
103	1800	5·32	4·19	15·2	1·25	3·66	9·10	n.a.	n.a.	n.a.	n.a.	n.a.	0·000	0·840	0·137	—	—	—	6·60	19·2	2·91	—	—
134	1800	3·51	4·50	12·7	0·653	3·74	5·23	0·280	0·007	0·016	n.a.	n.a.	0·000	0·706	0·122	0·848	0·046	0·106	13·1	36·4	2·78	(0·97)	—
149	1800	4·07	4·84	15·2	0·707	5·18	5·01	0·470	0·009	0·025	n.a.	n.a.	0·000	0·670	0·136	0·865	0·036	0·099	15·7	46·4	2·96	1·18	2·54
154	1800	4·59	4·74	16·0	0·768	5·86	4·41	0·670	0·015	0·040	0·015	0·010	0·002	0·642	(0·165)	0·848	0·041	0.110	18·4	57·8	3·14	1·41	2·44
161	1800	3·40	3·46	13·3	0·660	4·75	4·22	0·810	0·020	0·060	0·035	0·030	0·004	0·674	0·142	0·820	0·045	0·135	19·3	61·3	3·18	2·34	3·82
162	7200	4·18	4·20	13·3	0·554	5·26	3·46	1·01	0·018	0·064	0·035	0·030	0·004	0·656	0·142	0·850	0·033	0·117	20·7	59·0	2·85	2·50	4·24
164	7200	3·09	3·71	10·9	0·448	4·01	2·88	1·00	0·020	0·065	0·035	0·030	0·004	0·632	0·133	0·843	0·037	0·120	22·3	64·2	2·88	2·63	4·10
175	5400	3·63	3·45	11·4	0·437	4·78	2·25	1·61	0·030	0·080	0·080	0·070	0·007	0·617	(0·159)	0·872	0·035	0·093	29·8	84·8	2·85	3·66	4·32
175	7200	4·07	4·16	11·9	0·388	4·90	1·96	1·93	0·035	0·112	0·080	0·070	0·007	0·577	0·141	0·858	0·034	0·108	27·6	87·4	3·17	3·59	4·11
														mean values	0·137	0·851	0·038]	0·111					
															±0·017	±0·037	±0·012	±0·027					

The units of k_2, k_3, k_6, k_7, k_{7c}, k_{8e}, k_{8c} and k_{8c} are cm³/molecule sec; the units of k_8 are sec⁻¹.

(M = $[R_{C_2H_6}+R_{C_4H_{10}}]/R_{CO}$; n.a. means not analyzed.)

Fig. 1 and 2 are the corresponding Arrhenius plots for these results. The energies of activation differ slightly from those given in the preliminary communication [36]; the revised values are based upon a larger number of experiments and a more comprehensive mechanism. Measurement of the rate of reaction (9) was attempted only at 164 and 175°C; the corresponding values of $10^{-4}\, k_9 k_2^{\frac{1}{2}}/k_{6c}$ are 4·4 and 8·2 molecule$^{\frac{1}{2}}$ cm$^{-3/2}$ sec$^{-\frac{1}{2}}$, respectively, and the values of $k_8 k_{6c}/k_9 k_{7c}$ are 6·1 and 4·5, respectively.

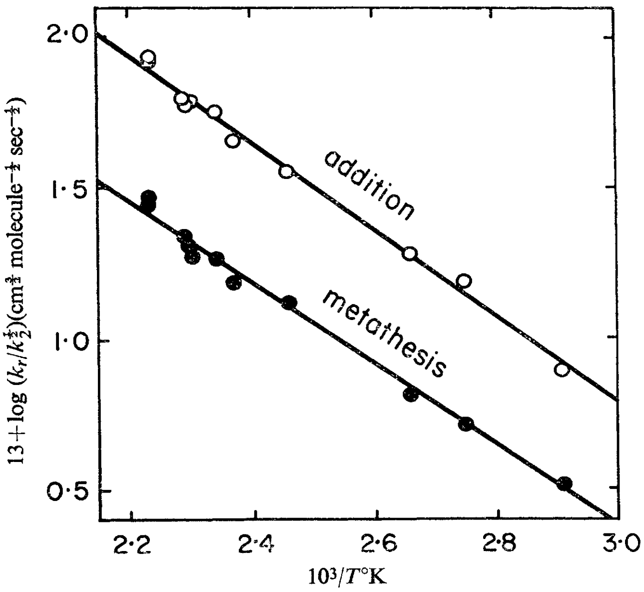

Fig. 1.—Addition and metathesis between the ethyl radical and diallyl. The activation energy for addition is 6·6±0·4 kcal/mole; for metathesis, 6·3±0·4 kcal/mole.

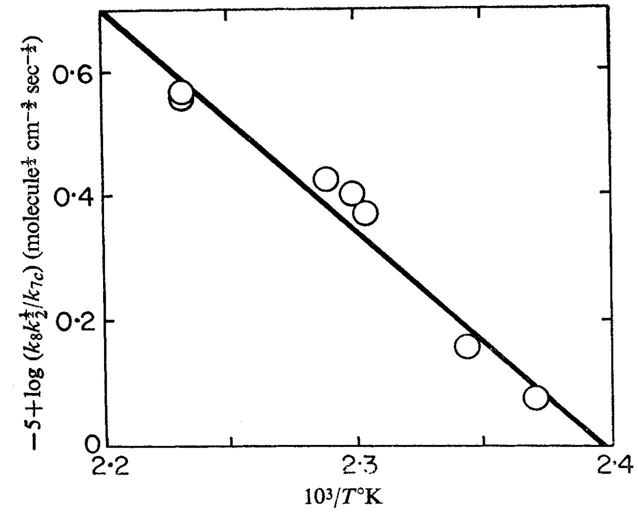

Fig. 2.—The dismutation of the adduct radical: $C_8H_{15}^{\bullet} \rightarrow C_5H_{10}+C_3H_5^{\bullet}$; the activation energy is 16±4 kcal/mole.

The value for k_7/k_6 indicates that the diallyl molecule is significantly more reactive towards the ethyl radical in addition than in metathesis, and this difference is expressed significantly only in the pre-exponential factor. A parallel, but much more pronounced difference has been found with allyl acetate,[37] where metathesis with the ethyl radical is too slow for measurement. The magnitude of this difference appears to be linked with the degree of shielding afforded by the substituent group to the reactive hydrogen atoms of the methylene group. The activation energies of metathesis and addition for diallyl are both slightly but significantly lower for diallyl than for octene-1, for which $E_6 - \frac{1}{2}E_2 = 7{\cdot}5 \pm 0{\cdot}5$ kcal/mole,[31] and $E_7 - \frac{1}{2}E_2 = 7{\cdot}6 \pm 0{\cdot}2$ kcal/mole.[38] The activation energy of the dismutation reaction (8) does not differ significantly for diallyl (16·4 ± 4·0 kcal/mole) and for allyl acetate (15·4 ± 1·3 kcal/mole),[37] but the rate constant at 150°C is significantly higher for the latter, the values of $\log (k_8 k^{\frac{1}{2}}/k_{7c})$ being 6·27 ± 0·22 for allyl acetate and 5·12 ± 0·11 for diallyl, corresponding to a factor of 14 in the rate constants.

The mutual disproportionation-combination ratio for ethyl radicals, k_3/k_2, was found to be 0·137 ± 0·017 in this investigation, in good agreement with the recent value of 0·137 ± 0·010 measured in a similar photolysis of diethyl ketone in the presence of octene-1.[31]

The estimation of the disproportionation processes (8*d*) and (8*e*) is based upon the assumption that we may neglect the reactions of the allyl radical with diallyl:

$$C_3H_5^{\bullet} + C_6H_{10} \rightarrow C_3H_6 + C_6H_9^{\bullet} \tag{6a}$$

$$C_3H_5^{\bullet} + C_6H_{10} \rightarrow C_9H_{15}^{\bullet}. \tag{7a}$$

The energies of activation for these reactions should exceed those for reactions (6) and (7) by an amount approximately equal to the delocalization energy Q of the allyl radical. The most reliable estimate of Q seems to be 12·6 ± 0·8 kcal/mole; moreover this is most probably a minimum value for Q.[39] The corresponding ratios k_{6a}/k_6 and k_{7a}/k_7 will be given approximately by $\exp(-Q/RT)$, which has the value 10^{-6} at 175°C, and we conclude that reactions (6*a*) and (7*a*) are indeed negligible under our conditions. We may therefore assume that the only source of propene in the system is reaction (8*e*), that allyl radicals are consumed entirely by reactions (8*c*), (8*d*) and (8*e*), and that the relative rates of these reactions may properly be calculated from the appropriate equations of the previous section.

The results of table 1 reveal the patterns of combination and disproportionation shown by the allyl radical between 134 and 175°C:

$$\begin{aligned}
[CH_2 \mathrel{\overset{\textstyle -}{-}} CH \mathrel{\overset{\textstyle -}{-}} CH_2]^{\bullet} + {}^{\bullet}CH_2CH_3 &\rightarrow C_5H_{10} && (85 \pm 4)\,\%;\ [90\,\%] \\
&\rightarrow CH_2{=}C{=}CH_2 + CH_3CH_3 && (4 \pm 1)\,\%;\ \ [3\,\%] \\
&\rightarrow CH_3CH{=}CH_2 + CH_2{=}CH_2 && (11 \pm 3)\,\%;\ [7\,\%]
\end{aligned}$$

and by the vinyl radical between 161 and 175°C:

$$\begin{aligned}
CH_2{=}CH^{\bullet} + {}^{\bullet}CH_2CH_3 &\rightarrow C_4H_8 && (87 \pm 3)\,\%;\ [94\,\%] \\
&\rightarrow CH{\equiv}CH + CH_3CH_3 && (10 \pm 3)\,\%;\ [2\,\%] \\
&\rightarrow 2CH_2{=}CH_2 && (3 \pm 1)\,\%;\ \ [4\,\%]
\end{aligned}$$

Limits of error are given at the 5 % probability level. The values in square brackets have been estimated by the equation of Holroyd and Klein[35]:

$$\log (k_{\text{dis}}/k_{\text{com}}) = 0{\cdot}131(\Sigma S^{\circ}_{\text{dis}} - S^{\circ}_{\text{com}}) - 5{\cdot}47.$$

The agreement between the measured and predicted values is fairly good for the allyl radical, but poor for the vinyl radical.

Disproportionation between allyl and ethyl radicals is not negligibly small. Disproportionation between α-allyl allyl radicals and ethyl radicals was also detected; as suggested in the previous section, the primary products were tentatively identified as the cis and trans isomers of hexatriene-1,3,5:

$$\begin{aligned} &CH_3CH_2^{\bullet} + [CH_2 \mathrel{\overset{\scriptscriptstyle ---}{-}} CH \mathrel{\overset{\scriptscriptstyle ---}{-}} CH.CH_2CH=CH_2]^{\bullet} \\ &\quad \rightarrow CH_3CH_3 + \text{trans-}CH_2=CH.CH=CH.CH=CH_2 \\ &\quad \rightarrow CH_3CH_3 + \text{cis-}CH_2=CH.CH=CH.CH=CH_2 \end{aligned}$$

and, of these, only the cis form isomerizes to cyclohexadiene-1,3: [33, 34]

$$\text{cis-}CH_2=CH.CH=CH.CH=CH_2 \rightarrow \text{cyclo-}C_6H_8\text{-1,3}.$$

The percentage of the α-allyl allyl radicals to undergo disproportionation is equal to 100 $R_{C_6H_8}/R_6$, which has the value 0·41 at 91°C and 0·40 at 164°C. Clearly, disproportionation is far less important for the α-allyl allyl radical than for the allyl radical. The pattern of disproportionation can be obtained directly from the ratio $R_{\text{cis}}/R_{\text{trans}} = 2{\cdot}7$ at 91°C, and indirectly from the ratio $(R_{\text{cis}}+R_{\text{cyclo}})/R_{\text{trans}} = 3{\cdot}0$ at 164°C, where the subscripts indicate the nature of C_6H_8 product estimated. We conclude that the less stable cis isomer of hexatriene-1,3,5 is formed 3 times as rapidly as the trans isomer in the disproportionation between α-allyl allyl and ethyl radicals. No evidence could be found for the formation of α-allyl allene, another possible product of this disproportionation reaction.

The interactions of the allyl and ethyl radicals may be compared with the corresponding reactions of the allyl and methyl radicals:

$$\begin{aligned} &[CH_2 \mathrel{\overset{\scriptscriptstyle ---}{-}} CH \mathrel{\overset{\scriptscriptstyle ---}{-}} CH_2]^{\bullet} + {}^{\bullet}CH_3 \rightarrow CH_2=CHCH_3CH_3 && (c) \\ &\qquad\qquad \rightarrow CH_2=C=CH_2 + CH_4. && (d) \end{aligned}$$

Unfortunately allene was not identified in two recent studies of the reactions of the methyl radical with propene.[17, 29] Nevertheless allene has been shown to be a significant product of the mercury photosensitized decomposition of propene,[40] butene-2 [41] and pentene-1.[42] The propene and butene-2 systems have been studied in the presence of a large excess of methyl-d_3 radicals, which act as efficient scavengers of the primary radical species. Allene and 1-butene-4-d_3 were found among the products in the ratio of 0·06 in the propene system, and of 0·14 in the butene-2 system. These results show that allyl radicals are formed in the primary process, and the ratios may be taken as an estimate of k_d/k_c appropriate to the particular conditions of each experiment. Such estimates are high in comparison with the value of 0·023 predicted by the equation of Holroyd and Klein,[35] but this difference is not unexpected. The interaction of propyl and methyl-d_3 radicals has been studied under parallel conditions,[43] and the corresponding value of k_d/k_c estimated as 0·5, which is 3 times as great as the accepted value of 0·17. A propyl radical formed by the transfer of the triplet state energy of the mercury atom to a propane molecule should possess several quanta of vibrational energy initially. Disproportionation may occur before deactivation is complete, leading to the abnormally high values of k_d/k_c, as suggested in footnote (3) of ref. (43). If similar arguments are applied to the estimates of k_d/k_c given above for the allyl radical, we may conclude that the predicted value of 0·023 is of a reasonable order of magnitude for the interaction of thermally equilibrated allyl and methyl radicals.

The upper limit of 0·01 assigned to k_d/k_c for the mutual interaction of two allyl radicals deserves some comment. This estimate was obtained at 750°C, some 600° above the temperatures of this investigation. Recent studies of the interaction of two ethyl radicals [44] and of two isopropyl radicals [45] in the gas phase have indicated an apparent difference between the energies of activation for combination and disproportionation of 0·4 and 0·3 kcal/mole respectively. This difference causes k_d/k_c to increase as the temperature is decreased, and the increase for a drop of 600°C is considerable; indeed, Holroyd and Klein's equation predicts that k_d/k_c should be 0·07 at 25°C. Further study of the mutual interaction of allyl radicals and of the interaction of allyl and methyl radicals is clearly desirable, and we are extending the method of this investigation to the study of these systems.

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