897. *The Reaction of Methyl Radicals with Propene.*

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The reaction between $^{14}CH_3$ radicals and propene has been studied over the temperature range 150—480°. The proportion of methyl radicals which react to give methane and an allyl radical increases with temperature, and at 480° almost all react in this way. Allyl radicals attack propene much less readily than do methyl radicals. Appreciable amounts of [1-^{14}C]propene are formed by the interaction of $^{14}CH_3$ radicals and inactive propene above 390°, while the specific activity of the methane formed decreases with increasing temperature. Estimations of ^{14}C activity were made by scintillation counting of gas samples, and the advantages of this technique are stressed. The bearing of the results on the mechanism of the inhibition of chain reactions by propene is discussed.

The rate of the thermal decomposition of many substances such as hydrocarbons and ethers is reduced to a more or less defined limit by the addition of nitric oxide or propene. The nature of the reactions proceeding under conditions of maximum inhibition is of great interest. A good deal of evidence suggests that the rate of the fully inhibited reaction is essentially that of a distinct molecular rearrangement.[1] On the other hand observations of the extent of isotopic mixing during the pyrolysis of mixtures of normal and deuterium-substituted hydrocarbons in the presence of inhibitors suggest that chain processes may still be taking place in the presence of sufficient inhibitor to reduce the rate to its minimum value.[2] Moreover, the rate of decomposition of many substances is observed to increase again in the presence of amounts of inhibitor greater than those required for maximum inhibition. The processes responsible for this increase have not been established.

In order to acquire more information about the precise mechanism of the inhibition itself and about the reactions taking place under conditions of maximum inhibition, a study has been made of the interaction of $^{14}CH_3$ radicals with propene under a variety of conditions.

Experimental

The apparatus used for the kinetic measurements was similar to that previously described.[3] Measurements of ^{14}C activity were made by direct scintillation counting of gas samples. For this purpose the samples were transferred by Toepler pump to a small cell (30 ml.) provided with a plane Perspex window 1½ in. in diameter attached by wax to a flange. A disk of plastic scintillator material (Pamelon, by Isotope Developments Ltd.), 1 mm. thick, was held in contact with the inner surface of the window. The outer face could be placed in contact with the window of an end-on photomultiplier (Type 6097A by E.M.I. Ltd.) housed in a light-tight box screened by 2 in. of lead. Optically clear paths were obtained by the use of a drop of silicone oil between the faces in contact. The electronic counting equipment consisting of cathode-follower, amplifier, discriminator, and scaling unit was conventional; a similar equipment has been described by Stranks.[4] Gas-scintillation counting has decisive advantages over other techniques for estimations of ^{14}C activity in volatile organic materials, but seems to have been almost entirely neglected. The observed rates of count were accurately proportional to sample pressure up to at least 50 mm. The fact that the gas samples are not chemically changed or mixed with any other substance makes it easy to recover the whole of the active material after counting. When dealing with mixtures it is possible to treat the sample with a suitable reagent for the removal of one component and then return the remainder to the cell

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[1] Jach, Stubbs, and Hinshelwood, *Proc. Roy. Soc.*, 1954, *A*, **224**, 283; Hinshelwood, *Chem. Soc. Special Publ.* No. 9, 1957, p. 49.

[2] Rice and Varnerin, *J. Amer. Chem. Soc.*, 1954, **76**, 324; Kupperman and Larson, *J. Chem. Phys.*, 1960, **33**, 1264.

[3] Danby and Hinshelwood, *Proc. Roy. Soc.*, 1942, *A*, **179**, 169.

[4] Stranks, *J. Sci. Instr.*, 1956, **33**, 1.

for a second estimation of activity. The activity of each component is thus determined directly. This technique has been extensively employed in the present work.

50 mm. of [1,3-$^{14}C_2$]acetone containing a convenient level of activity were mixed with various pressures of propene and photolysed for a time corresponding to about 15% decomposition. The contents of the reaction vessel were then drawn through a trap at −185°. The uncondensed fraction (methane, carbon monoxide, and hydrogen) was passed into a bulb of known volume, and its pressure was measured. It was then pumped into the scintillation counting cell and its activity measured. The composition of the fraction was determined by mass-spectrometric analysis of the products of identical experiments carried out with inactive acetone.

The material condensed in the trap was then warmed to −80° and the components volatile at this temperature were pumped off. The activity of this fraction was determined as before by scintillation counting, after the removal of traces of acetone by treatment with 2,4-dinitrophenylhydrazine. The sample was then removed from the counting cell and treated with mercuric perchlorate solution to remove olefins, and the residual activity was measured. In some experiments the C_3 fraction was separated by gas-chromatography before the radiochemical estimation.

Results and Discussion

The results of a series of experiments covering a wide range of propene pressures and at temperatures from 150° to 480° are given in Tables 1—3. Propene can react with methyl radicals in two ways:

$$CH_3\cdot + CH_3\cdot CH{=}CH_2 = CH_4 + \cdot CH_2\cdot CH{=}CH_2 \quad (1)$$

$$CH_3\cdot + CH_3\cdot CH{=}CH_2 = \text{Butyl radical} \quad (2)$$

Between 100° and 300° the following process accounts satisfactorily for the photolysis of acetone:[5]

$$CH_3\cdot CO\cdot CH_3 + h\nu = 2CH_3\cdot + CO \quad (3)$$

$$2CH_3\cdot = C_2H_6 \quad (4)$$

$$CH_3\cdot + CH_3\cdot CO\cdot CH_3 = CH_4 + \cdot CH_2\cdot CO\cdot CH_3 \quad (5)$$

$$CH_3\cdot + \cdot CH_2\cdot CO\cdot CH_3 = CH_3\cdot CH_2\cdot CO\cdot CH_3 \quad (6)$$

$$2\text{-}CH_2\cdot CO\cdot CH_3 = (CH_2\cdot CO\cdot CH_3)_2 \quad (7)$$

Methyl radicals and carbon monoxide are only formed in reaction (3). Therefore the measurement of the amount of carbon monoxide formed enables the number of methyl radicals released, and hence the total amount of ^{14}C contained in the products to be calculated (column 3 of Table 1).

When [^{14}C]acetone is photolysed the methyl radicals produced will have the same specific activity as the original acetone, and measurements of the activity of the different products of the interaction of such radicals with propene will indicate their fate directly. Propene competes for methyl radicals by reactions (1) and (2) and in the presence of sufficient propene the reactions (4), (5), and (6) are no longer significant. No ethyl methyl ketone could be detected mass-spectrometrically in the products of the photolysis of acetone at 150° in the presence of as little as 20 mm. of propene. The rate of formation of ethane decreased to zero as the propene pressure increased. At 150° in the presence of propene the following additional reactions can take place:

$$CH_3\cdot + \text{Allyl} = \text{Butyl} \quad (8)$$

$$CH_3\cdot + \text{Butyl} = \text{Isopentane} \quad (9)$$

$$\text{Butyl} + C_3H_6 = C_7 \text{ radical} \quad (10)$$

$$\text{Allyl} + C_3H_6 = C_6 \text{ radical} \quad (11)$$

$$\text{Butyl} + C_3H_6 = \text{Butane} + \text{Allyl} \quad (12)$$

$$\text{Butyl} + \text{Allyl} = \text{Heptene} \quad (13)$$

$$\text{Butyl} + \text{Butyl} = \text{Octane} \quad (14a)$$

$$\text{(or Butane + Butene)} \quad (14b)$$

$$\text{Allyl} + \text{Allyl} = \text{Biallyl} \quad (15)$$

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[5] Dorfman and Noyes, *J. Chem. Phys.*, 1948, **16**, 788.

TABLE 1.

Distribution of activity in the products of photolysis of [1,3-$^{14}C_2$]acetone in the presence of propene.

(Initial acetone pressure 50 mm.)

				Distribution of activity in products *			
Temp.	Initia C_3H_6 (mm.)	CO formed (10^{-2} mmoles)	Total activity in products (10^{-6} mc)	CH_4	Unsatd. products up to C_5	Satd. products up to C_5	Involatile polymers
150°	0·0	3·03	107	17·4	57·5		25·1
	0·0	3·01	107	20·1	56·1		23·8
	10·0	2·93	104	20·3	5·0	49·6	25·2
	25·0	2·92	103	17·8	7·4	41·1	33·7
	49·4	3·01	107	17·7	11·1	27·5	43·7
	91·0	2·86	101	16·5	11·0	17·5	55·1
	199·9	2·85	101	13·4	—	13·2	—
286°	0·0	2·45	87	60·5	15·1		24·4
	10·2	2·46	87	48·6	14·9	11·4	25·2
	25·8	2·53	90	40·4	20·0	16·4	23·1
	50·3	2·14	76	29·5	25·3	19·1	26·2
	100·8	3·14	111	20·1	30·6	13·9	35·3
	199·5	2·03	72	19·1	39·7	18·4	22·8
	301·0	1·54	54	23·6	—	26·6	—
390°	0·0	1·17	41	70·1	12·1		17·8
	10·1	1·15	41	66·0	20·7		13·3
	50·4	0·92	33	61·3	—		—
	100·0	1·22	43	56·4	33·8 †	5·6	4·1
	199·2	1·16	41	42·4	38·1	10·2	9·3
	301·0	1·09	39	42·3	40·2	13·2	4·3

* These figures are expressed as a percentage of the activity of the acetone decomposed, calculated from the CO formed, it being assumed that each molecule of acetone yields one molecule of CO.

† 41·4% of activity in this fraction was in propene.

TABLE 2.

Distribution of activity in products of photolysis of [1,3-$^{14}C_2$]acetone in the presence of propene at 480°C.

(Initial acetone pressure 50 mm.)

			Distribution of activity in products *		
Initial C_3H_6 (mm.)	CO formed (10^{-2} mmoles)	Total activity in products (10^{-6} mc.)	CH_4	Unsatd. products up to C_5	Satd. products up to C_5
0·0	0·59	20·9	134·5	—	
9·8	0·70	24·6	96·9	37·3	
25·2	0·84	29·9	77·0	43·1	1·8
52·6	0·85	30·2	76·2	43·3	2·8
102·7	0·79	28·1	63·2	39·8 †	3·1
191·8	0·81	28·7	56·4	50·0	1·4
304·2	0·89	31·6	49·9	49·1	4·8

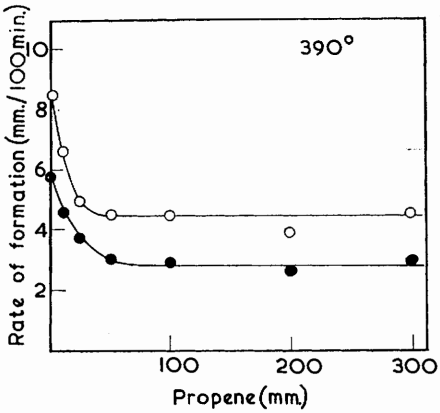
* See Table 1.

† 52·2% of activity in this fraction was in propene.

Reaction (9) is in competition with (1), (2), and (12), all of which involve propene. The amount of isopentane formed would therefore be expected to increase with increasing propene pressures to a maximum and then to decrease at still higher propene pressures. This is observed (Table 3).

The rate of formation of carbon monoxide is not affected by the presence of propene up to 286°. Below this temperature all the observed products are accounted for by the reaction scheme given above. In calculating the total activity in the products as given in Tables 1 and 2 it has been assumed that the number of carbon monoxide molecules formed is equal to the number of acetone molecules decomposed. This assumption appears satisfactory up to 390°. At 480°, however, the activity found in the volatile products alone exceeds that computed on this basis. It is clear that the rate of formation of carbon monoxide is no longer a reliable measure of the rate of photolysis at this temperature, probably owing to the formation of keten polymers. The decomposition of the acetonyl radical to give keten has been reported by Ferris and Haynes.[6]

The rate of formation of carbon monoxide is reduced by propene at temperatures above 390° (Figs. 1 and 2) to a limiting value corresponding to the rate of reaction (3). We can therefore assume that under these conditions the formation of acetonyl by reaction (5) is negligible because virtually all the methyl radicals are consumed by reaction with propene or by radical combinations such as reaction (8). This is demonstrated by the fact that the total activity in the products (sum of columns 4—6 in Table 2) approaches the total activity calculated from the amount of carbon monoxide formed as the propene pressure increases. The amount of carbon monoxide formed can therefore still be taken as a measure of the number of methyl radicals released in reaction (3). At 480° the amount of propene required to reduce the rate of formation of carbon monoxide from 50 mm. of acetone to a limit is about 50 mm. This amount of propene reduces the amount of activity found in the products of low molecular weight (up to C_5) to about the value calculated on the assumption that reaction (3) is the only source of carbon monoxide.



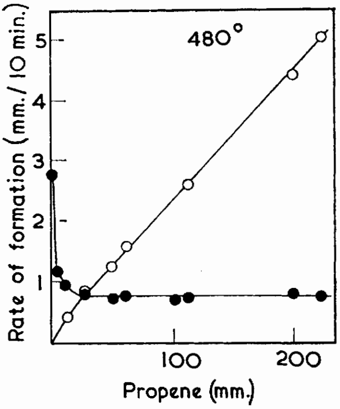


FIG. 1. Effect of propene on rates of formation of methane and carbon monoxide in acetone photolysis, at 390°. ○ methane; ● carbon monoxide.

FIG. 2. Effect of propene on rates of formation of hydrogen and carbon monoxide in acetone photolysis at 480°. ● carbon monoxide; ○ hydrogen × 10.

If methyl radicals were formed only in reaction (3) the specific activity of the methane from reaction (1) or (5) should be independent of the propene pressure. This is observed up to 286° (Fig. 3). At higher temperatures the specific activity of the methane decreases with increasing propene pressure. The activity of the methyl radicals, and hence of methane derived from them, will be reduced if butyl radicals formed from the addition of $^{14}CH_3$ radicals to propene decompose by loss of inactive methyl radicals. The results given in Tables 1 and 2 show that a substantial amount of *active* propene is present in the products of the reaction of $^{14}CH_3$ radicals with inactive propene, indicating that this radical-exchange process is important. Processes of this kind have also been observed by Varnerin[7] and by McNesby and Gordon.[8] The instability of the butyl radical at 480° is shown by the fact that no butane is found. Chain-transfer reactions involving radicals larger than C_4H_9 will also lead to a reduction in methyl-radical specific activity. Evidence

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[6] Ferris and Haynes, *J. Amer. Chem. Soc.*, 1950, **72**, 893.
[7] Varnerin, *J. Amer. Chem. Soc.*, 1954, **77**, 1426.
[8] McNesby and Gordon, *J. Amer. Chem. Soc.*, 1957, **79**, 4593.

for such processes is given, for example, by the low mean molecular weight of the polymers formed in radical-induced olefin polymerisation at 300°.[3]

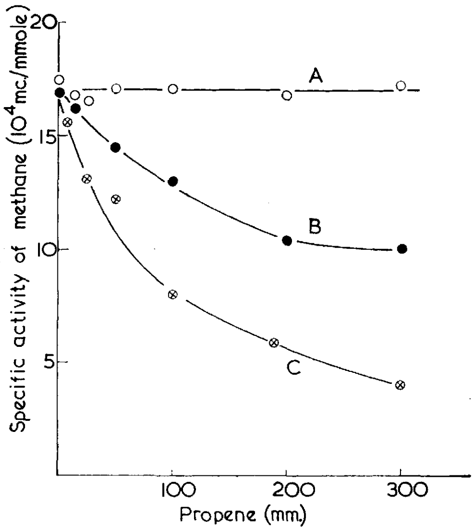

FIG. 3. Effect of propene on specific activity of methane from photolysis of [1,3-$^{14}C_2$]-acetone.

A, 286°; B, 390°; C, 480°.

If methyl radicals and carbon monoxide were formed only in reaction (3) the CH_4 : CO ratio could not exceed 2. At 480° in the presence of 330 mm. of propene this ratio rises to 4·6. The specific activity of the methane must, therefore, also be affected by the formation of inactive methyl radicals or methane from other sources. Chain-transfer

TABLE 3.

Products volatile at −80° from photolysis of acetone in the presence of propene.

(Initial acetone pressure: 50 mm.)

Temperature 150°. *Time of reaction* 3·5 *hr.*

Initial propene pressure (mm.) ...	0·0	22·0	49·9	100·2	200·8	489·5
Isopentane	—	1·7	1·3	1·1	0·5	0·0
Pentenes	—	0	0	0	0·3	1·0
Butenes	—	0·9	1·2	1·1	1·0	1·2
Ethane	4·5	2·4	1·2	0·5	0·1	0·0

Temperature 286°. *Time of reaction* 140 *min.*

Initial propene pressure (mm.) ...	0·0	53·5	97·1	130·0	172·2	295·9	503·7
Pentenes	—	0·9	1·6	1·7	2·0	2·4	3·5
Butenes	—	3·5	4·8	5·3	5·8	7·3	8·4
Ethane	0·6	1·4	1·6	1·5	1·9	1·8	1·7
Ethylene	0·2	0·8	1·0	0·6	1·5	0·6	—

Temperature 390°. *Time of reaction* 126 *min.*

Initial propene pressure (mm.) ...	0·0	50·0	99·8	199·1
Pentadienes	—	0·4	0·2	1·2
Pentenes	—	0·2	0·1	0·6
n- and Iso-butane	—	0·6	0·8	1·6
Butenes	—	1·6	2·0	3·5
Propane	—	0·5	0·6	1·9
Ethane	—	0·5	0·9	1·5
Ethylene	0·4	0·6	2·6	3·5

Temperature 480°. *Time of reaction* 45 *min.*

Initial propene pressure (mm.) ...	0·0	25·5	111·9	201·3
Pentadienes	—	0·6	0·6	1·4
Butenes	—	1·3	2·6	3·3
Propane	—	0·2	2·1	3·3
Ethane	0·2	0·4	0·8	1·5
Ethylene	0·6	1·2	4·2	7·2

processes involving large radicals formed by the addition of allyl radicals to propene will give inactive methyl radicals:

$$\text{Allyl} + C_3H_6 = C_6 \text{ radical} = CH_3 + \text{Pentadiene} \qquad (17)$$

Considerable amounts of pentadienes are in fact observed in the products formed at higher temperatures (Table 3). The increasing amounts of propane and ethylene formed at the higher temperatures and the appearance of hydrogen at 480° are evidence for processes such as:

$$H + C_3H_6 = C_3H_7\cdot \qquad (18)$$

$$C_3H_7\cdot = C_2H_4 + CH_3\cdot \qquad (19)$$

$$C_3H_7\cdot + C_3H_6 = C_3H_8 + C_3H_5\cdot \qquad (20)$$

Inactive methane could also arise directly by pyrolysis of propene. It was shown that no measurable decomposition took place at 390° but that it was detectable at 480° (Table 4). The rate of formation of methane from this source was much too slow to account for an appreciable proportion of the inactive methane observed.

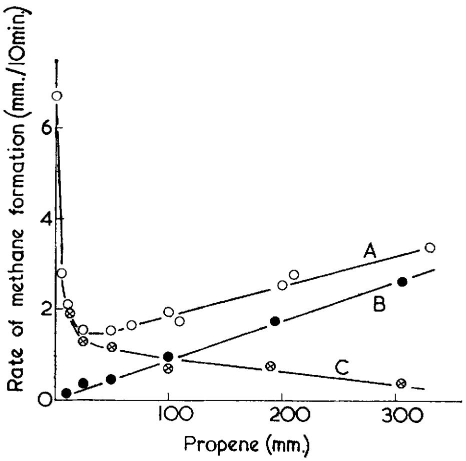

FIG. 4. Effect of propene on rate of formation of methane in acetone photolysis at 480°.
A, Total methane;
B, inactive methane;
C, active methane.

The measurement of the specific activity of the methane formed at 480° in the presence of various concentrations of propene makes it possible to resolve the curve showing the overall rate of methane formation into two components giving the rates of formation of active and inactive methane separately (Fig. 4). The rate of formation of inactive methane is directly proportional to propene pressure. That of active methane falls extremely rapidly with quite small additions of propene. At higher propene pressures the rate continues to fall, but much more slowly. There is thus strong evidence for the chain-transfer process discussed above. Reaction (2), therefore, fails to cause inhibition at higher temperatures because of the intervention of chain-transfer processes which regenerate methyl radicals. This conclusion is supported by the observation that the proportion of the active methyl radicals which appear in the final products as methane increases with temperature. At higher temperatures, therefore, reaction (1) becomes

TABLE 4.

Products of the pyrolysis of propene at 480°.

(Time of reaction: 45 min.)

Initial propene pressure (mm.)	100	200	300
Methane (mm.)	0·6	2·2	5·1
Hydrogen (mm.)	0·2	0·7	1·4
$10^5 \times CH_4/(\text{Propene})^2$	6·0	5·5	5·5
CH_4/H_2	3·4	3·4	3·6

progressively more effective than reaction (2) as a means of removing methyl radicals. Reaction (1) results in the replacement of methyl by allyl. If allyl radicals were completely inert, or if they could only react in chain-ending steps such as reactions (8), (13), or (15), the effect of propene would be to suppress chain processes completely. It is clear from the experimental results that at temperatures up to about 300° this mechanism will apply. The rate of any residual reaction occurring under these conditions in the presence of sufficient propene is therefore unambiguously that of a molecular rearrangement. At higher temperatures pentadienes appear in the products. These can only arise by processes such as (17) in which a chain-carrying radical is regenerated. However, the reactivity of allyl is substantially less than that of the radical whose interaction with propene led to its formation. For this reason propene effectively inhibits the rates of many higher-temperature pyrolyses. However, the continued presence of allyl radicals in such systems has been demonstrated and their interaction with the substance being pyrolysed, although probably slow, cannot be discounted.

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