476. *The Reaction of Methyl Radicals with Olefins. Part II. The Comparison of the Reactivity of Different Olefins.*

By F. A. Raal and C. J. Danby.

When acetaldehyde vapour is irradiated with ultra-violet light at 300° in the presence of different olefins, the photolysis is inhibited to an extent which increases with increasing molecular weight of the olefin, and more markedly as the number of methyl groups on the olefinic carbon atoms is increased. The rate of polymerisation of the higher olefines is small and becomes independent of olefin pressure as soon as the latter exceeds a small value. The ease of the primary interaction of methyl radicals with olefins does not vary greatly with the nature of the olefin, and the increasing inhibition is due to a greater tendency of the higher olefins to give products which are unable to undergo chain transfer.

Danby and Hinshelwood (*Proc. Roy. Soc.*, 1941, *A*, **179**, 169) investigated the kinetics of the photolysis of acetaldehyde in the presence of ethylene, propylene, and *iso*butylene. Their results have been confirmed and the series of olefins extended to include butene-1, butene-2, trimethylethylene, tetramethylethylene, and hexene-1.

Experimental Methods.

The experimental arrangements were the same as those described in the preceding paper. All experiments were carried out at 300°. The olefins were prepared as follows.

Propylene.—*iso*Propyl alcohol was dehydrated with phosphoric oxide.

iso*Butylene.*—*tert.*-Butyl alcohol was dehydrated with 30% sulphuric acid (by volume) or by anhydrous oxalic acid.

Butene-1.—This was made by the action of alcoholic potash on *n*-butyl iodide.

Butene-2.—*sec.*-Butyl alcohol was carefully dehydrated with phosphoric oxide.

The above olefins are gases at room temperature and were dried by passage through phosphoric oxide and fractionated between cooled traps, only the middle fractions being collected. Infra-red analysis of the butene-2 showed it to be substantially free from butene-1.

Trimethylethylene.—*tert.*-Amyl alcohol was dehydrated by 50% sulphuric acid (by volume). The distillate was washed with 10% sodium hydroxide and with water, and after being dried ($CaCl_2$) was fractionated (b. p. 36—38°).

Tetramethylethylene.—Methyl *tert.*-butyl ketone was prepared from acetone by way of pinacol hydrate (*Org. Synth.*, Coll. Vol. I, 448) and reduced with sodium to methyl-*tert.*-butylcarbinol (Richard, *Ann. Chim.*, 1910, [viii], **21**, 346), which was then dehydrated with anhydrous oxalic acid. The tetramethylethylene was separated by steam-distillation, dried, and fractionated (b. p. 72—74°).

Hexene-1.—Allyl bromide was added very slowly to a solution of propylmagnesium bromide in dry ether, and after decantation from the solid residue most of the ether was removed by distillation. The remaining ether was eliminated by repeated washing with water, and the olefin dried ($CaCl_2$) and fractionated (b. p. 61—63°) (*J. Amer. Chem. Soc.*, 1918, **40**, 832). Infra-red analysis showed that all the double bonds in the product were terminal.

EXPERIMENTAL RESULTS.

The initial rate of photolysis and the rate of the induced polymerisation were measured at 300° with 50 mm. acetaldehyde and various amounts of the different olefins. Fig. 1 shows the results for the inhibition of the aldehyde photolysis by ethylene, butene-2, trimethylethylene, and tetramethylethylene. Fig. 2 gives the rate of the induced polymerisation as a function of olefin pressure, the marked points in these figures being the experimental values, and the curves being *calculated* from equations I and II of the preceding paper. Similar curves were obtained for the other olefins. The values of the constants C and $\frac{1}{2}nK$ which give the closest agreement with experiment are given in Table I.

TABLE I.

Values of the constants C *and* ½nK *which give the closest agreement with experiment when substituted in equations I and II.*

Olefin.	C.	$\frac{1}{2}nK$.
Ethylene	8.01×10^{-4}	3.85×10^{-4}
Propylene	1.00×10^{-2}	7.2×10^{-3}
*iso*Butylene	1.06×10^{-2}	6.6×10^{-3}
Butene-1	1.10×10^{-2}	8.0×10^{-3}
Butene-2	1.12×10^{-2}	6.3×10^{-3}
Trimethylethylene	1.65×10^{-2}	6.0×10^{-3}
Tetramethylethylene	2.24×10^{-2}	1.0×10^{-2}
Hexene-1	1.15×10^{-2}	3.0×10^{-3}

The values for ethylene and propylene are in good agreement with those obtained by Danby and Hinshelwood (*loc. cit.*). The extent of the inhibition of the acetaldehyde photolysis by *iso*butylene was somewhat less than that previously observed. The values given above were obtained with several different samples of *iso*butylene and are probably more reliable.

DISCUSSION.

The reaction scheme given in the preceding paper for the photolysis of acetaldehyde in the presence of ethylene leads to equations for the rate of photolysis of the aldehyde (equation I) and for the rate of the induced polymerisation (equation II). The results in Figs. 1 and 2 show that, with suitable choice of constants, these equations also give excellent agreement with the experimental results for the photolysis of acetaldehyde in the presence of the higher olefins, suggesting that the same reaction mechanism adequately describes these reactions. Quantitative information about the relative values of the velocity constants of the individual reactions with different olefins may be derived from the values of the constants given in Table I.

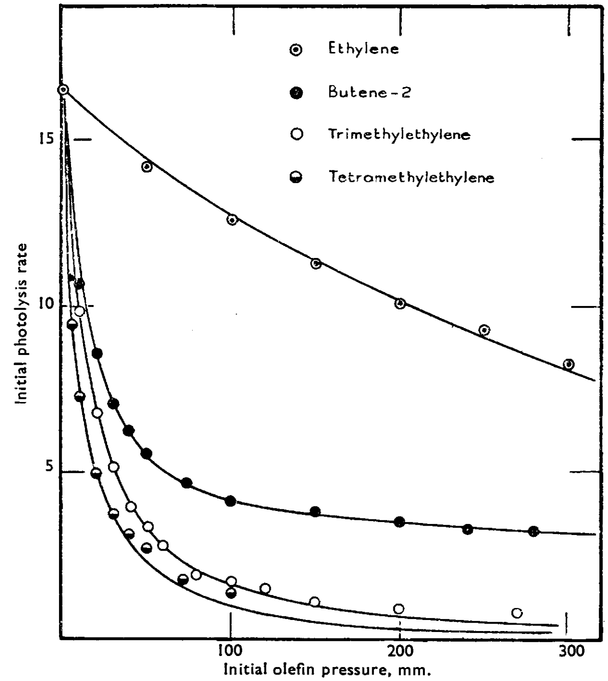
Danby and Hinshelwood showed that for ethylene the value of the constant n was approximately 3; with the higher olefins no great error is introduced by assuming a standard value $n = 2$ for these reactions. From the values of C and $\frac{1}{2}nK$ in Table I we can then calculate a series of values for the ratio k_4/k_2 for :

$$C = k_2k_4\beta/2k_3, \text{ and } K = (k_4)^2\beta/k_3$$

whence $K/2C = k_4/k_2$.

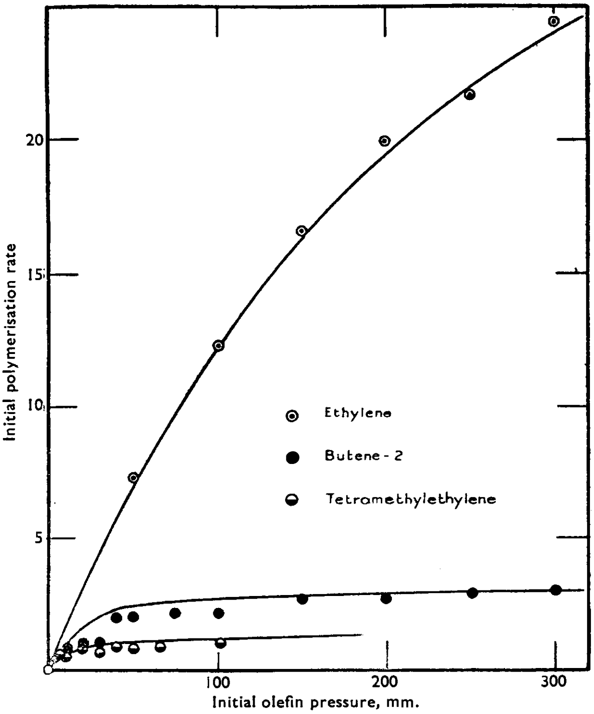
The ratio k_4/k_2 gives a value for the ease of interaction of a methyl radical with the olefin, compared with that for its interaction with acetaldehyde. The relatively small differences in the value of k_4/k_2 shown in Table II suggest that there are no major variations in the ease with which methyl radicals attack the different olefins. The markedly greater inhibition of the aldehyde photolysis produced by the higher olefins—and more particularly by those having more than one methyl group attached to the olefinic carbon atoms—is therefore not to be attributed to an increased tendency of these olefins to absorb methyl radicals.

FIG. 1.



Inhibition of the photolysis of 50 *mm. acetaldehyde by various olefins. The curves are those* calculated *from equation I with the values of* C *given in Table I.*

FIG. 2.



Rates of polymerisation of olefins induced by photolysis of 50 *mm. of acetaldehyde. The curves are those* calculated *from equation II with the values of* C *and* $\frac{1}{2}$nK *given in Table I.*

From the expressions for C and K given above, $\beta = \frac{4\,k_3\,C^2}{(k_2)^2\,K}$. Values of β, and hence of the ratio k_7/k_6 may be obtained from this expression by the method used by Danby and Hinshelwood.

TABLE II.

Olefin.	k_4/k_2.	β.	k_7/k_6.
Ethylene	0·16	0·055	0·06
Propylene	0·36	0·30	0·43
*iso*Butylene	0·31	0·37	0·59
Butene-1	0·36	0·33	0·49
Butene-2	0·28	0·43	0·75
Trimethylethylene	0·18	0·98	49·0
Tetramethylethylene	0·22	1·0	∞
Hexene-1	0·13	0·95	19·0

(Because of the very small extent of polymerisation observed with tri- and tetra-methylethylene the value of the constant $\frac{1}{2}nK$ for these olefins is known to a rather lower degree of precision. The corresponding data in the above table are shown bracketed.)

This requires an estimate of the chain length of the photolysis of acetaldehyde under the conditions of the experiment. By extrapolation from the results of Mitchell and Hinshelwood (*Proc. Roy. Soc.*, 1937, *A*, **159**, 32) a reasonable value for the chain length of photolysis of 50 mm. acetaldehyde at 300° is found to be 28 units. From this value, together with the data in Table I the approximate values for β and for k_7/k_6 given in Table II are obtained.

Several interesting conclusions may be drawn at once from these results. As explained above, the small variation in the value of the ratio k_4/k_2 in passing from ethylene to the higher olefins shows that the higher olefins do not in general react more readily with methyl radicals. On the other hand there is a striking increase in the value of the ratio k_7/k_6. This ratio gives a measure of the relative probability that a growing polymer radical should undergo chain termination rather than chain transfer. Whilst with ethylene only about one reaction chain in 20 fails to undergo chain transfer and regenerate a methyl radical, with the higher olefins there is only a small probability that chain transfer will occur.

The pronounced inhibition of the acetaldehyde photolysis produced by the more complex olefins is therefore to be attributed to the increasing tendency of the larger radicals to isomerise into a form which is unable either to continue the polymerisation by addition of fresh olefin molecules or to continue the kinetic chain by the process of methyl-radical chain transfer.

PHYSICAL CHEMISTRY LABORATORY, OXFORD.

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