176. *The Reactions of Alkyl Radicals. Part IX.* The Addition of Methyl, Ethyl, Isopropyl, and t-Butyl Radicals to Acetylene and the Isomerization of Alkenyl Radicals.*

By J. A. Garcia Dominguez and A. F. Trotman-Dickenson.

The *A* factors and activation energies for addition of alkyl radicals to acetylene have been studied in systems in which the radicals have been produced by photolysis of the appropriate aldehydes and found to be:

	log *A* (c.c. mole^{-1} sec.$^{-1}$]	*E* (kcal. mole^{-1})		log *A* (c.c. mole^{-1} sec.$^{-1}$)	*E* (kcal. mole^{-1})
Me	11·4	7·7	Pr^{i}	11·2	6·9
Et	11·0	7·0	Bu^{t}	10·7	5·3

The alkenyl radicals formed by addition of isopropyl and t-butyl radicals isomerize by movement of a methyl group.

The only attempt to measure the rate of addition of an alkyl radical to acetylene in the gas phase that can be regarded as sufficiently based on product analyses is that of

---

* Part VIII, Metcalfe and Trotman-Dickenson, *J.*, 1960, 5072.

Mandelcorn and Steacie.[1] They employed the material-balance method to study the reaction of methyl radicals. We have now used the method devised to study the addition of radicals to ethylene earlier in this series.[2] When an aldehyde is photolysed in the presence of acetylene, the following reactions, among others, could be expected to occur:

$$\mathrm{R{\cdot}CHO} + h\nu \longrightarrow \mathrm{R{\cdot}} + \mathrm{{\cdot}CHO}$$

$$\mathrm{R{\cdot}} + \mathrm{R{\cdot}CHO} \longrightarrow \mathrm{RH} + \mathrm{{\cdot}CRO} \tag{1}$$

$$\mathrm{{\cdot}CRO} \longrightarrow \mathrm{R{\cdot}} + \mathrm{CO} \tag{2}$$

$$2\mathrm{R{\cdot}} \longrightarrow \mathrm{R_2} \tag{3}$$

$$\mathrm{R{\cdot}} + \mathrm{C_2H_2} \longrightarrow \mathrm{R{\cdot}CH{:}CH{\cdot}} \tag{4}$$

$$\mathrm{R{\cdot}CH{:}CH{\cdot}} + \mathrm{R{\cdot}CHO} \longrightarrow \mathrm{R{\cdot}CH{:}CH_2} + \mathrm{{\cdot}CRO} \tag{5}$$

Ethyl and larger radicals will also undergo disproportionation.

Hydrogen atoms formed from formyl radicals can be expected to react either with the aldehyde or with acetylene. In neither eventuality will the presence of atoms seriously complicate the system. From the reaction scheme, it can be shown that

$$R_{\mathrm{R{\cdot}CH{:}CH_2}} = k_4[\mathrm{R}][\mathrm{C_2H_2}]$$

and

$$R_{\mathrm{R_2}} = k_3[\mathrm{R}]^2$$

where $R_{\mathrm{R{\cdot}CH{:}CH_2}}$ is the rate of formation of the olefin. Hence $k_4 = k_3^{\frac{1}{2}} R_{\mathrm{R{\cdot}CH{:}CH_2}}/R_{\mathrm{R_2}}^{\frac{1}{2}}[\mathrm{C_2H_2}]$. k_3 for methyl radicals is known, so that the rate constant for addition can be found by analysis for propene and ethane. Unfortunately the reaction system is not as straightforward as the scheme indicates. Some of the alkenyl radicals will react with acetylene to give, eventually, some diolefin. The concentrations of acetylene and acetaldehyde must be chosen so that the amounts of these higher products are very small. Conditions were adjusted so that they amounted to less than 3%, as far as could be determined by analysis. Some compounds with more than six carbon atoms may have escaped detection.

The Addition of Methyl Radicals.—The results of the runs are summarized in the Table.

The addition of methyl radicals to acetylene.

Temp. (°K)	Time (sec.)	$[\mathrm{C_2H_2}]$	$[\mathrm{C_2H_2}]/[\mathrm{Ald.}]$	$R_{\mathrm{C_2H_6}}$	$R_{\mathrm{C_3H_6}}$	$\log (k_4/k_3^{\frac{1}{2}})$
370·8°	900	1·28	2·12	7·53	5·34	0·183
375·0	900	1·77	2·47	8·47	8·16	0·199
376·0	1800	1·95	1·65	11·75	10·83	0·210
378·6	1080	2·14	1·97	32·44	18·83	0·190
385·2	900	2·33	2·51	10·67	17·56	0·364
385·6	900	1·79	1·77	38·93	19·46	0·242
395·5	900	1·27	0·96	18·52	17·80	0·439
410·4	900	1·36	2·46	12·24	16·63	0·543
411·2	720	1·99	1·76	17·66	35·31	0·626
413·5	900	1·25	0·97	24·63	25·11	0·584
430·8	900	1·00	0·94	17·58	25·74	0·784
431·0	900	0·93	1·55	10·05	17·89	0·784
433·2	1800	0·515	1·00	9·73	8·79	0·738
434·0	960	1·33	1·66	13·53	29·72	0·782
434·5	900	1·54	2·46	6·59	29·20	0·870
434·5	1200	0·864	0·69	18·32	23·54	0·803
458·5	1020	0·646	0·78	12·46	24·92	1·039
478·8	900	1·87	1·69	14·75	107·30	1·175

$[\mathrm{C_2H_2}]$ and [Ald.] are the concentrations of acetylene and aldehyde in 10^{-6} mole cm.$^{-3}$. Rates of formation of products are given as 10^{-12} mole c.c.$^{-1}$ sec.$^{-1}$. Rate constants are in c.c. mole^{-1} sec.$^{-1}$.

In addition to ethane and propene the products at higher temperatures contained propane and hydrocarbons containing four and five carbon atoms. Together they amounted to

---

[1] Mandelcorn and Steacie, *Canad. J. Chem.*, 1954, **32**, 79.

[2] Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572.

1—3% of the main products. There was no peak attributable to an alkenyl dimer. No benzene was found though a careful search was made because Drew and Gordon[3] found it at higher temperatures. The runs yield:

$$\log k_4 \text{ (c.c. mole}^{-1}\text{ sec.}^{-1}) = 11{\cdot}4 - (7700/2{\cdot}3\boldsymbol{R}T)$$

if $$\log k_3 \text{ (c.c. mole}^{-1}\text{ sec.}^{-1}) = 13{\cdot}3 \text{ (cf. ref. 4)}$$

Mandelcorn and Steacie[1] found

$$\log k_4 = 11{\cdot}0 - (5500/2{\cdot}3\boldsymbol{R}T),$$

using the material balance method which is likely to err, if at all, in yielding a high value for k_4.

The Addition of Ethyl Radicals.—This reaction was also studied between 100° and 200°; the concentration of acetylene was between 0·73 and 2·43 × 10^{-6} mole c.c.$^{-1}$, and $[C_2H_2]$/[Propionaldehyde] between 0·62 and 3·67. The moderate scatter of the points was not systematic. Very small chromatographic peaks that might have been due to hydrocarbons with five carbon atoms were observed. There was also a larger peak which was not identified; its position corresponded to that of an unsaturated hydrocarbon with six carbon atoms, but not benzene; its area was small and varied irregularly. The rate constant calculated from the but-1-ene and n-butane from 20 runs is:

$$\log k_4 \text{ (c.c. mole}^{-1}\text{ sec.}^{-1}) = 11{\cdot}0 - (7000/2{\cdot}3\boldsymbol{R}T)$$

on the assumption that $\log k_3$ (c.c. mole^{-1} sec.$^{-1}$) = 14.

The Addition of Isopropyl Radicals.—The only hexane formed was 2,3-dimethylbutane, but pent-1-ene was formed as well as the expected 3-methylbut-1-ene. Both olefins were identified by their retention times on the chromatographic column, which were compared with those of known compounds, and by their infrared spectra. For the purposes of determining the rate of addition the rates of production of the two olefins were added together. The Arrhenius equation for k_4 was found from 21 runs in which the total pressure was 50—100 mm. Within this range $[C_2H_2]$/[isobutyraldehyde] was 0·8—4·8.

Between 90° and 204°

$$\log k_4 \text{ (c.c. mole}^{-1}\text{ sec.}^{-1}) = 11{\cdot}2 - (6900/2{\cdot}3\boldsymbol{R}T)$$

if $\log k_3 = 14$. Runs at 200 and 350 mm. indicate that the high-pressure rate constant is probably 30% higher than that given above, because the rate of addition is slightly influenced by the need for collisional deactivation of the alkenyl radical when it is first formed exothermically. This matter was not fully investigated. A few runs in which the actinic light was filtered through a sheet of Pyrex glass also gave results that were about 30% high.

The Addition of t-Butyl Radicals.—The analytical system was not suitable for the accurate determination of 2,2,3,3-tetramethylbutane. The concentrations of t-butyl radicals were therefore deduced from the rate of formation of isobutene and the known ratio of the rate constants for disproportionation and combination which was taken as 4·38.[5] An allowance was made for the isobutene from the decomposition of the radical formed in the abstraction of a hydrogen atom from the alkyl group of pivalaldehyde.[5] The rate of addition was found from the sum of the rates of formation of 3,3-dimethylbut-1-ene and 4-methylpent-1-ene, which were identified by gas chromatography and by their infrared spectra. Twenty runs between 100° and 220° with the concentration of

---

[3] Drew and Gordon, *J. Chem. Phys.*, 1959, **31**, 1417.
[4] Shepp, *J. Chem. Phys.*, 1956, **24**, 939.
[5] Birrell and Trotman-Dickenson, *J.*, 1960, 4218.

acetylene between 0·373 and 13·1 × 10^{-6} mole c.c.$^{-1}$ and the concentration of aldehyde between 0·36 and 1·55 × 10^{-6} mole c.c.$^{-1}$ yielded

$$\log k_4 \text{ (c.c. mole}^{-1}\text{ sec.}^{-1}) = 10{\cdot}7 - (5300/2{\cdot}3RT)$$

if

$$\log k_3 \text{ (c.c. mole}^{-1}\text{ sec.}^{-1}) = 14.$$

Arrhenius plots for the four addition reactions are shown in Fig. 1.

The Isomerization of Alkenyl Radicals.—At high pressures 3,3-dimethylbut-1-ene is the only olefin formed by addition of t-butyl radicals, and 95% of the olefin from isopropyl radicals is 3-methylbut-1-ene. Fig. 2 shows how the reduction of pressure in the system leads to 4-methylpent-1-ene and pent-1-ene, respectively, in the products. These compounds could have been formed from isobutyl and n-propyl radicals if the original radicals had isomerized. If isopropyl radicals isomerized, n-hexane and 2-methylpentane would have been found in the products. No trace of either was detected even under conditions where more than 50% isomerization would have been needed to explain the results. Further, the reactions of isopropyl and t-butyl radicals have several times been studied by other workers, who have not reported isomerization.[6] Accordingly it must be the alkenyl radical, in either its incipient or final form, that isomerizes. The observed products can only be obtained if a methyl group migrates; they cannot come from the shift of a hydrogen atom which might be regarded as a faster process. The addition of an alkyl radical to acetylene is about 30 kcal. mole^{-1} exothermic. This energy is apparently sufficient to overcome the barriers to isomerization if it is not removed by collision. The experiments in the presence of nitrogen (Fig. 2) show that collision with a small molecule will deactivate the radical though the relative efficiency is, as would have been expected, low. They also show that the pressure effect is not dependent on the reactivity of the gases present. The results were not sufficiently accurate to show any difference in the deactivation efficiences of the acetylene and the aldehydes.

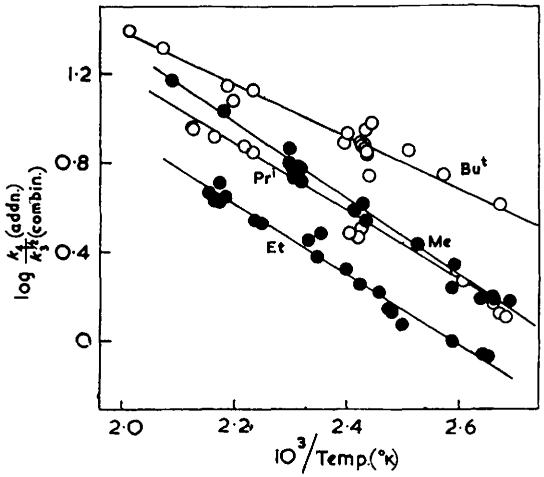

FIG. 1. Arrhenius plots for the addition of methyl, ethyl, isopropyl, and t-butyl radicals to acetylene.

Several runs with both isopropyl and t-butyl radicals were carried out at low pressures over a range of temperatures. Plots of the logarithms of the proportions of olefins formed from isopropyl radicals against the reciprocal temperature showed greater isomerization at high temperatures and were markedly curved. Runs with t-butyl radicals at total pressures of 30, 40, and 50 mm. also showed marked temperature coefficients. The isopropyl plots flattened at low temperatures, as would be expected if most of the energy for isomerization came from the exothermicity of the addition. The rate of isomerization

---

[6] For references see Kerr and Trotman-Dickenson, " Progress in Reaction Kinetics," Pergamon Press, Oxford, 1961, Vol. I, p. 105.

was unaltered when isopropyl radicals were initially formed by photolysis of isobutyraldehyde with light filtered through Pyrex glass. Isomerization might be expected to yield an equilibrium mixture of the radicals. If the free energies of formation of the alkenyl radicals follow those of the hydrocarbons with an additional hydrogen atom, the more highly branched radical is rather more stable than the isomer that is formed. There is no apparent tendency at the lowest pressures to form an equilibrium mixture of products with the more highly branched olefin in slight excess.

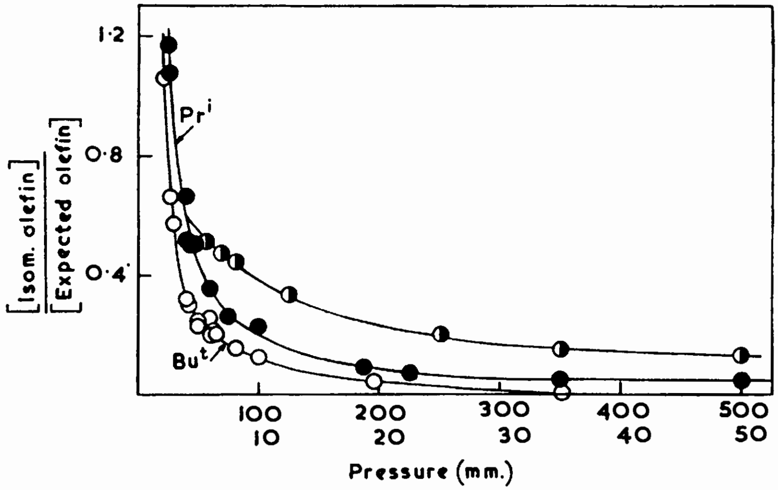

FIG. 2. The variation, with pressure, of the proportion of isomerized olefin in the products of the addition of alkyl radicals to acetylene.

● Pent-1-ene/3-methylbut-1-ene from the photolysis of isobutyraldehyde in acetylene (~1 : 1 mixtures).

◑ Pent-1-ene/3-methylbut-1-ene from the photolysis of 20 mm. of isobutyraldehyde in 20 mm. of acetylene with added nitrogen, at 406° ± 4°K.

○ 4-Methylpent-1-ene/3,3-dimethylbut-1-ene from the photolysis of pivalaldehyde in acetylene (~1 : 1 mixtures) at 410°K (lower scale).

The formation of the additional olefins from both isopropyl and t-butyl radicals is the first definite evidence for the isomerization of small hydrocarbon radicals, about which there has been considerable discussion.[6]

Experimental.—The apparatus and procedure were substantially the same as those employed formerly in this series. The light source was a 125-w mercury arc. The products were passed through both the usual aldehyde absorbent and an acetylene absorbent made from 25% by weight of a saturated solution of silver nitrate in ethylene glycol on 20—30 mesh firebrick.

Materials. B.D.H. acetaldehyde, propionaldehyde, and isobutyraldehyde were purified by bulb-to-bulb distillation with rejection of head and tail fractions. Koch's pivalaldehyde was purified by gas chromatography. Acetylene (B.O.G.) was freed from non-condensable gases.

Analysis. Products were analysed by gas chromatography on a temperature-programmed alumina column with 1% of squalane as a tailing reducer. Hydrogen was the carrier gas. The detector was a thermal-conductivity gauge. Its sensitivity was determined by measurement of the areas of the peaks obtained on the recorder chart from measured samples of ethane, propene, butane, isobutene, isopentane, 2,3-dimethylbutane, and 4-methylpent-1-ene. The results showed that the sensitivities for alkenes and alkanes of the same carbon number were identical.

Acknowledgment for a grant is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society.

CHEMISTRY DEPARTMENT, EDINBURGH UNIVERSITY. [*Received, August* 21*st*, 1961.]