1269. *Preparation and Reactions of Vinyl Radicals*

By N. A. Weir

Vinyl radicals have been prepared by the methyl-radical sensitised decompositions of acraldehyde and vinyl formate; attempts to obtain the radicals directly by photolyses of acraldehyde and divinylmercury were unsuccessful. Ratios of rate constants (Δ) for like- and cross-disproportionation to like- and cross-combination, determined at 175°, are: Δ(Vinyl,Vinyl) = 1·1, Δ(Me,Vinyl) = 2·3.

ALTHOUGH a large amount of quantitative data is now available for the reactions of alkyl radicals,[1] comparatively little is known about the reactions of unsaturated radicals, possibly because of the difficulty in obtaining clean sources of these radicals, and also the problems of product analysis, *e.g.*, separation of alkene–alkyne mixtures.

Le Roy and Tickner [2] produced vinyl radicals from vinyl bromide and iodide by using the sodium diffusion flame technique, and obtained rates of production of acetylene, ethylene, and butadiene, the products of vinyl-radical disproportionation and combination. From these results, a value of 0·5 can be calculated for Δ(Vinyl,Vinyl), the rate-constant ratio for disproportionation to combination. This technique is, however, of limited accuracy, and the purpose of the present work was to investigate alternative sources of vinyl radicals and to study their reactions.

Several standard sources of alkyl radicals are available, and the corresponding vinyl compounds were examined. Attempts to photolyse divinylmercury were unsuccessful, negligible amounts of hydrocarbons being formed even on prolonged irradiation with the unfiltered output of a medium-pressure mercury arc at 275°. Under such conditions the

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[1] J. A. Kerr and A. F. Trotman-Dickenson, " Progress in Reaction Kinetics," Pergamon, Oxford, 1961, p. 107.

[2] D. J. Le Roy and A. W. Tickner, *J. Chem. Phys.*, 1951, **19**, 1247.

mercury alkyls decompose readily, and it appears that the vinyl groups confer on this molecule considerable stability to ultraviolet irradiation.

Similar treatment of acraldehyde yielded large amounts of ethylene and only very small amounts of acetylene and butadiene, indicating that in the initial photolytic act the molecular decomposition, $CH_2{:}CH{\cdot}CHO \longrightarrow C_2H_4 + CO$, predominates. The vinyl-radical concentration is thus not sufficiently high to effect appreciable sensitised decomposition of the aldehyde.

Sensitised decomposition of acraldehyde was achieved by using methyl radicals produced by the selective photolysis of acetone in the presence of acraldehyde. Similar treatment of vinyl formate, however, yielded much lower concentrations of vinyl radicals, suggesting that the bond-dissociation energy of the formyl C–H is greater than that of the aldehyde C–H. Satisfactory yields of vinyl radicals were obtained from vinyl formate

$$CH_3{\cdot}CO{\cdot}CH_3 + h\nu = 2CH_3{\cdot} + CO$$

$$CH_3{\cdot} + CH_2{:}CH{\cdot}CHO = CH_2{:}CH{\cdot}CO{\cdot} + CH_4$$

$$CH_2{:}CH{\cdot}CO{\cdot} = CH_2{:}CH{\cdot} + CO$$

$$(CH_3)_3CO{\cdot}CO(CH_3)_3 = 2CH_3{\cdot} + CH_3{\cdot}CO{\cdot}CH_3$$

$$CH_3{\cdot} + H{\cdot}CO_2{\cdot}CH{:}CH_2 = CH_4 + CH_2{:}CH{\cdot}CO_2{\cdot}$$

$$CH_2{:}CH{\cdot}CO_2{\cdot} = CO_2 + CH_2{:}CH{\cdot} \tag{1}$$

$$2CH_3{\cdot} = C_2H_6$$

$$2CH_2{:}CH{\cdot} = C_2H_2 + C_2H_4 \tag{2}$$

$$2CH_2{:}CH{\cdot} = C_4H_6 \tag{3}$$

$$CH_3{\cdot} + CH_2{:}CH{\cdot} = CH_4 + C_2H_2 \tag{4}$$

$$CH_3{\cdot} + CH_2{:}CH{\cdot} = C_3H_6 \tag{5}$$

$$CH_2{:}CH{\cdot}CO_2{\cdot} = CO_2 + CH_2{:}CH{\cdot} \tag{6}$$

$$CH_2{:}CH{\cdot}CO_2{\cdot} = CO + CH_2{:}CH{\cdot}O{\cdot} \tag{7}$$

when higher methyl-radical concentrations were used, the methyl radicals being produced by the themal decomposition of di-t-butyl peroxide. The Scheme accounts adequately for the observed reaction products. The decomposition of the vinylcarboxyl radical [reaction (1)] requires explanation. Two mechanisms, (6) and (7), are possible. Although the heat of formation of the vinylcarboxyl radical is unknown, the difference in ethalpy changes for reactions (6) and (7) can be found by using standard thermochemical data and values of 65 kcal.mole^{-1} (ref. 3) and 20 kcal.mole^{-1} (calculated from Skinner's data [4]) for heats of formation of vinyl and vinyloxy radicals, respectively. Reaction (7) is at least 22 kcal. mole^{-1} more endothermic than (6), and thus the decomposition shown in (1) will be thermochemically favoured, a fact that was borne out by product analysis; carbon dioxide, but no unsaturated oxygenated compounds like alcohols, being detected.

It is conceivable that some decomposition of vinyl radicals into acetylene and hydrogen atoms will occur.

Using the above thermochemical data it can be shown that the activation energy for such a process will be about 40 kcal. mole^{-1}, and it can therefore be concluded that, at the temperatures employed in this investigation, vinyl-radical decomposition will not be important; thus, total acetylene production can be accounted for by reactions (2) and (4).

The following relationship between disproportionation–combination ratios and observed rates of hydrocarbon formation can be derived.

Total rate of acetylene production

$$\begin{aligned} &= R(C_2H_2) = R(C_2H_2)\ (2) + R(C_2H_2)\ (4) \\ &= \Delta(\text{Vinyl,Vinyl})R(C_4H_6) + \Delta(\text{Me,Vinyl})R(C_3H_6) \end{aligned}$$

or

$$R(C_2H_2)/R(C_4H_6) = \Delta(\text{Vinyl,Vinyl}) + \Delta(\text{Me,Vinyl})\{R(C_3H_6)/R(C_4H_6)\}$$

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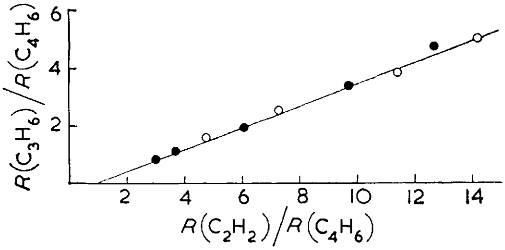
[3] A. G. Harrison and F. P. Lossing, *J. Amer. Chem. Soc.*, 1960, **82**, 519.

[4] H. A. Skinner, *Trans. Faraday Soc.*, 1963, **59**, 322.

A series of experiments was carried out at 175°, and the corresponding rates of hydrocarbon formation were obtained; the results are shown in the Figure. A least-mean-squares analysis of the data gives values of 1·1 and 2·3 for Δ(Vinyl,Vinyl) and Δ(Me,Vinyl), respectively. It can be seen that, although good agreement exists between the results obtained from the sensitised decompositions of the formate and aldehyde, agreement with Le Roy and Tickner's value for Δ(Vinyl,Vinyl) is not so good. It is possible that this discrepancy is due to the occurrence of heterogeneous reactions in the diffusion flame.



● Sensitised decomposition of acraldehyde using methyl radicals from acetone photolysis

○ Sensitised decomposition of vinyl formate using methyl radicals from di-t-butyl peroxide pyrolysis

EXPERIMENTAL

Appearance and Procedure.—The reactions were carried out in a 175-c.c. cylindrical quartz vessel housed in a coaxial furnace the temperature of which was maintained to within ±1° by means of a contact thermometer-activated relay unit. The cell was illuminated with the output from a 125 w medium-pressure mercury arc, and in the acetone photolysis a Corning filter, No. 054, was interposed between the arc and cell to limit the radiation to wavelengths greater than 3000 Å.

The cell was connected to a conventional high-vacuum system which incorporated reactant-storage and analytical sections. The analytical system consisted of a series of traps, a Toepler pump, gas-burette, and a gas-chromatographic unit; greaseless stopcocks were used throughout. After degassing the reactants, mixtures were prepared and introduced into the reaction vessel. The pressure of acetone and di-t-butyl peroxide used were 50 mm., while acraldehyde and vinyl formate pressures varied from 50 to 20 mm. After reaction, the products and unused reactants were transferred to the analytical system where, by means of cold traps, they were separated into condensable and non-condensable fractions. The non-condensable fraction, a mixture of carbon monoxide and methane, was pumped into the gas-burette and measured.

The condensable fraction was transferred to the gas-chromatographic injection system which was cooled in liquid air boiling under reduced pressure. Analyses were carried out at 0°, using a 15-ft. spiral glass column (5 mm. o.d.) packed with 40—60 mesh Celite containing 15% w/w of dimethylsulpholan; hydrogen was used as carrier gas at a flow rate of 44 c.c. min.$^{-1}$. The detector was a Gow-Mac thermal conductivity cell (type 9285) and its output was passed through an attenuator to a 0—1 mv Honeywell-Brown recorder. The column was calibrated by using standard samples of pure hydrocarbons.

Materials.—Acetone and di-t-butyl peroxide were purified by several bulb-to-bulb distillations, and were shown by gas chromatography to be pure. Acraldehyde (B.D.H.) and vinyl formate (Borden Chemical Company) contained impurities and were purified on the dimethylsulpholan column.

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EDWARD DAVIES CHEMICAL LABORATORY, UNIVERSITY COLLEGE, ABERYSTWYTH.
[Present address: CHEMISTRY DEPARTMENT, HERIOT-WATT COLLEGE,
CHAMBERS STREET, EDINBURGH 1.]
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