Free Radical Addition to Olefins. Part 23.† Kinetics of the Addition of Chloroiodomethane to Ethylene and Vinyl Fluoride

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The gas phase reaction of CH_2ClI with ethylene and vinyl fluoride, initiated photochemically and thermally with di-t-butyl peroxide, has been investigated, and the relative rates of addition of chloromethyl radicals to both ends of vinyl fluoride have been determined over a range of temperatures. The mechanism of the reaction is discussed, and the relative Arrhenius parameters for addition to the two alkenes are interpreted in terms of frontier orbital coefficients.

THE kinetics and orientation of addition to olefins has been studied for a number of radicals, but for the most part these have been electrophilic polyhalogenated species.[1] Methyl radicals show a sharp contrast to the

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† Part 22. H. C. Low, J. M. Tedder, and J. C. Walton, *Internat. J. Chem. Kinetics*, 1978, **10**, 325.

[1] J. M. Tedder and J. C. Walton, *Accounts Chem. Res.*, 1976, **9**, 183.

more electronegative species, both in their selectivity and reactivity, and this has been attributed to polar effects.[1,2] It is desirable to extend the work to other more nucleophilic radicals in order to gain a clearer understanding of the factors controlling the addition reaction.

Attempts to study the kinetics of addition to higher alkyl radicals, by chain addition of alkyl iodides to alkenes, were not successful,[3] since the iodine abstraction step in the chain propagation is endothermic and 1 : 1 adducts are not formed. However, the peroxide initiated addition of chloroiodomethane to alkenes in sealed tubes gave substantial amounts of adducts,[4] suggesting that the system was suitable for kinetic study. The chloromethyl radical is intermediate in polarity between methyl and fully halogenated species like trichloromethyl or trifluoromethyl radicals, and would provide, therefore, a valuable link between the two sets of data. In this paper we report a study of the gas-phase addition of chloromethyl radicals to ethylene and vinyl fluoride.

RESULTS AND DISCUSSION

Photolysis of CH_2ClI with ethylene in a quartz reactor, using unfiltered light from a medium pressure mercury arc, gave four major products, CH_3Cl, CH_2Cl_2, CH_3I, and CH_2I_2, together with minor amounts of CH_2ClCH_2Cl, but no adducts. Under these conditions it appears that sufficient energy is supplied to produce excited chloromethyl radicals, $CH_2Cl\cdot^*$, which react mainly by abstracting hydrogen and chlorine (and iodine) from the starting material [reactions (1)—(3)].

$$CH_2ClI + h\nu \longrightarrow \cdot CH_2Cl^* + I\cdot \qquad (1)$$

$$\cdot CH_2Cl^* + CH_2ClI \longrightarrow CH_3Cl + \cdot CHClI \qquad (2)$$

$$\cdot CH_2Cl^* + CH_2ClI \longrightarrow CH_2Cl_2 + \cdot CH_2I \qquad (3)$$

It is possible that iodomethyl radicals are also formed in a competing primary step, and abstraction reactions of these radicals give rise to the latter two major products [reactions (4)—(6)]. The behaviour of CH_2ClI thus

$$CH_2ClI + h\nu \longrightarrow \cdot CH_2I + \cdot Cl \qquad (4)$$

$$\cdot CH_2I + CH_2ClI \longrightarrow CH_3I + \cdot CHClI \qquad (5)$$

$$\cdot CH_2I + CH_2ClI \longrightarrow CH_2I_2 + \cdot CH_2Cl \qquad (6)$$

parallels that of CH_3I which also gave no adducts, but only the abstraction products of excited methyl radicals under comparable conditions.[3]

In reactions initiated either thermally with di-t-butyl peroxide or photochemically with Pyrex-filtered light, the main products were 1 : 1 adducts of the chloromethyl radical and the olefin, accompanied by smaller amounts of the radical dimer, 1,2-dichloroethane. Methyl iodide and acetone were formed in comparable amounts in the peroxide initiated reactions (6) and (7). Acetone was found to be in slight excess in each case (see Table 1)

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)CO\cdot \longrightarrow CH_3\cdot + (CH_3)_2CO \qquad (6)$$

$$CH_3\cdot + CH_2ClI \longrightarrow CH_3I + \cdot CH_2Cl \qquad (7)$$

suggesting that a small proportion of the methyl radicals takes part in other reactions such as addition to the alkene. Methyl chloride was formed in the peroxide initiated reactions, and since it was not produced in the photochemical experiments, it seems probable that a small fraction of the primary methyl radicals abstract chlorine from CH_2ClI rather than iodine [reaction (8)].

$$\cdot CH_3 + CH_2ClI \longrightarrow \cdot CH_2I + CH_3Cl \qquad (8)$$

The methyl chloride analysis was not very accurate due to the small quantities produced, but it appears that methyl radicals abstract iodine *ca.* 20 times faster than chlorine from CH_2ClI.

Szwarc and his co-workers studied the reaction of methyl radicals with CH_2ClI in toluene solution[5] and found that iodine was abstracted *ca.* 500 times more rapidly than hydrogen at 65 °C. The technique employed would not have revealed the presence of chlorine abstraction. Szwarc's work with methyl radicals, and Whittle's gas phase studies of halogen abstraction by trifluoromethyl radicals,[6] showed that although iodine is abstracted from monohalogenoalkanes many orders of magnitude more rapidly than chlorine, the difference in the rates of abstraction of the two halogens decreases sharply with increasing halogen content in polyhalogenomethanes. The value of *ca.* 20 for the relative rate of iodine to chlorine abstraction found in the present study does not look unreasonable in the light of this earlier work.

The 1 : 1 adducts are formed in a straightforward chain reaction (9)—(11). The main termination is

$$\cdot CH_2Cl + CH_2{=}CH_2 \xrightarrow{k_{2e}} CH_2ClCH_2CH_2\cdot \xrightarrow{CH_2ClI} CH_2ClCH_2CH_2I \qquad (9)$$

$$\cdot CH_2Cl + CH_2{=}CHF \xrightarrow{k_{2n}} CH_2ClCH_2CHF\cdot \xrightarrow{CH_2ClI} CH_2ClCH_2CHFI \qquad (10)$$

$$\cdot CH_2Cl + CHF{=}CH_2 \xrightarrow{k_{2r}} CH_2ClCHFCH_2\cdot \xrightarrow{CH_2ClI} CH_2ClCHFCH_2I \qquad (11)$$

dimerization of the chloromethyl radical giving 1,2-dichloroethane, but other terminations such as combination of methyl with chloromethyl radicals cannot be ruled out in the peroxide initiated series. The relative rates of formation of the products from a competitive series of experiments using both ethylene and vinyl fluoride are given in Table 1. The good consistency of the rates of adduct formation with both thermal and

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[2] H. C. Low, J. M. Tedder, and J. C. Walton, *J.C.S. Faraday I*, 1976, 1300.

[3] J. M. Tedder and K. D. R. Winton, unpublished results.

[4] N. McMurray, J. M. Tedder, L. L. T. Vertommen, and J. C. Walton, *J.C.S. Perkin II*, 1976, 63.

[5] R. J. Fox, F. W. Evans, and M. Szwarc, *Trans. Faraday Soc.*, 1961, **57**, 1915.

[6] W. G. Alcock, and E. Whittle, *Trans. Faraday Soc.*, 1965, **61**, 244; 1966, **62**, 134, 664.

photochemical initiation is strong evidence that excited chloromethyl radicals are not important when Pyrex-filtered light is used.

TABLE 1

Relative rates of formation of products from the addition of chloroiodomethane to ethylene and vinyl fluoride

T/°C	t/h	$\frac{CH_3Cl}{CH_2ClCH_2CH_2I}$	$\frac{CH_3COCH_3}{CH_2ClCH_2CH_2I}$	$\frac{CH_3I}{CH_2ClCH_2CH_2I}$	$\frac{CH_2ClCH_2CHFI}{CH_2ClCH_2CH_2I}$	$\frac{CH_2ClCHFCH_2I}{CH_2ClCH_2CH_2I}$	$\frac{CH_2ClCH_2Cl}{CH_2ClCH_2CH_2I}$
103 (t)	22	0.03	0.59	0.43	0.26	0.045	0.063
121 (t)	22	0.05	0.73	0.67	0.25	0.042	0.11
135 (t)	22	0.06	0.99	0.73	0.26	0.055	
154 (t)	24	0.03	0.83	0.75	0.30	0.060	0.12
169 (t)	22				0.30	0.059	0.11
184	18				0.34	0.080	0.015
199	16				0.30	0.090	0.039
255	13				0.31	0.096	0.020

(t) Indicates thermal initiation with di-t-butyl peroxide; other runs initiated photochemically. Initial reactant concentrations were: $[CH_2ClI]$ 1.98 × 10^{-4}; $[CH_2{=}CH_2]$ 1.71 × 10^{-4}; $[CH_2{=}CHF]$ 3.12 × 10^{-4}; and $[Bu^tOOBu^t]$ 7.0 × 10^{-6}. A least squares plot of log (k_{2n}/k_{2e}) against 10^3 K/T gave a line with gradient -0.21 ± 0.18 and intercept -0.06 ± 0.06. A least squares plot of log (k_{2r}/k_{2e}) against 10^3 K/T gave a line with gradient -0.58 ± 0.23 and intercept 0.14 ± 0.10.

From the normal and reverse adducts of vinyl fluoride the orientation ratio $(k_{2r} : k_{2n})$ at 150 °C is found to be 0.20, which agrees well with the value found from sealed tube experiments.[4] The chloromethyl radical orientation ratio is virtually identical with that of methyl radicals (0.20 at 150 °C) and substantially different from that of trichloromethyl (0.07) or trifluoromethyl radicals (0.09).[1]

TABLE 2

Relative rates and Arrhenius parameters for addition of halogenomethyl radicals to vinyl fluoride

Radical	k_{2n}/k_{2e} at 164 °C	$\log(A_{2n}/A_{2e})$	$E_{2n} - E_{2e}$/kJ mol^{-1}	k_{2r}/k_{2e} at 164 °C	$\log(A_{2r}/A_{2e})$	$E_{2r} - E_{2e}$/kJ mol^{-1}	Ref.
$CH_3\cdot$	0.57	0.2	1.7	0.11	-0.7	1.3	2
$CH_2F\cdot$	0.56	-0.34	0.7	0.17			7
$CH_2Cl\cdot$	0.33	-0.06	3.8	0.07	0.14	10.9	This work
$CF_3\cdot$	0.48	-0.07	2.1	0.056	-0.29	8.0	1
$CCl_3\cdot$	0.56	-0.2	0.4	0.06	-0.2	8.8	1

Relative rates and pre-exponential factors are given per active site, *i.e.* the relative rates have been adjusted for the two sites available in ethylene. Subscript e refers to ethylene, n refers to the CH_2 site, and r refers to the CHF site in vinyl fluoride.

It can readily be shown from the mechanism that the relative rate constants for addition to the two alkenes are given by equation (12) provided reaction is limited

$$\frac{k_{2n}}{k_{2e}} = \frac{[CH_2ClCH_2CHFI]_f[CH_2{=}CH_2]}{[CH_2ClCH_2CH_2I]_f[CH_2{=}CHF]} \qquad (12)$$

to only a few percent consumption of the alkenes; a similar expression can be derived for $k_{2r} : k_{2e}$. Relative rate constants and Arrhenius parameters calculated from the data of Table 1 by the least squares procedure are compared with data for other radicals in Table 2.

Table 2 shows that all the radicals add more readily to ethylene than to the CH_2 site of vinyl fluoride and that they add *ca.* 10 times more rapidly to ethylene than to the CHF site. The A factor ratios do not differ greatly from unity for attack by the chloromethyl radical at either end of vinyl fluoride, as is the case for other radicals studied.[1] The decreased reactivity at the CHF end is primarily due to the higher enthalpy of activation for addition.

These results cannot be interpreted in terms of resonance delocalization of the unpaired electron in the adduct radical, because this would be expected to lead to a greater rate of reaction at CH_2 in vinyl fluoride than in ethylene, and about the same relative rate of reaction at CHF, which is contrary to the observed results. Consideration of the MO coefficients in the frontier orbitals of vinyl fluoride gives a more realistic model. Addition of halogenated electrophilic radicals like $CH_2Cl\cdot$ is controlled by the HOMO of the olefin. For vinyl fluoride the HOMO has the large coefficient on CH_2 so favouring normal addition. Nucleophilic radicals like $CH_3\cdot$, on the other hand, interact with the LUMO of a halogenated olefin. In the case of vinyl fluoride, where the LUMO has the large coefficient on CHF, reverse addition is favoured electronically. However, steric effects act to retard the rate of reverse relative to normal additions in unsymmetrical olefins, so the activation energy difference for addition to the two ends is much greater for electrophilic than nucleophilic radicals. This is amply demonstrated by the activation energies recorded in Table 2.

EXPERIMENTAL

Materials were obtained and purified as described previously,[4] and were handled on a conventional mercury-free vacuum line. Reactions were carried out in a cylindrical Pyrex cell (184 cm^3), apart from the preliminary experiments in a quartz cell of similar dimensions, and initiated with light from a Hanovia UVS 220 medium pressure mercury arc or thermally with di-t-butyl peroxide. The cell transmittance was monitored from time to time with a photomultiplier and remained unchanged throughout the series of experiments, indicating that transfer of

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[7] J. P. Sloan, J. M. Tedder, and J. C. Walton, *J.C.S. Perkin II*, 1975, 1846.

products for analysis was complete. The reaction cell was heated in an insulated furnace controlled by a Variac, which maintained the temperature constant to within ±2 °C. Product identification was achieved by coupled g.l.c.–mass spectrometry of the reaction mixtures using a Pye 104 gas chromatograph with a 4.6 m column of 25% w/w squalane on Chromasorb G, coupled *via* a single stage Biemann separator to an A.E.I. MS 902 mass spectrometer. The identity of CH_3Cl, CH_2Cl_2, CH_3I, CH_2I_2, CH_2ClCH_2Cl, and acetone was confirmed by retention time comparisons with authentic standards. Quantitative analysis was achieved using a gas chromatograph employing a Griffin and George gas density balance as detector, and using the same column as above. Peak areas were measured with a DuPont 310 curve resolver.

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