# Free Radical Addition to Olefins

Part 5.—Addition of Difluorobromomethyl Radicals to Trifluoroethylene and Ethylene

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The photochemical reaction of CF_2Br_2 with $CHF{=}CF_2$ and $CH_2{=}CH_2$ has been examined in a series of gas-phase experiments. A mechanism for the radical chain addition which takes place is proposed. The variation in the rate of formation of the termination products, CF_2BrCF_2Br and $CF_2BrCHFCF_2CF_2Br$, with reactant concentration is explained if five important termination reactions are taken into account and a long-lived excited state of the CF_2Br_2 is accepted. Arrhenius parameters for the addition of $CF_2Br\cdot$ radicals to the olefins have been derived :

$$CF_2Br\cdot + E \rightarrow CF_2BrE\cdot \qquad (2)$$

$$CF_2Br\cdot + CF_2Br\cdot \rightarrow CF_2BrCF_2Br. \qquad (4)$$
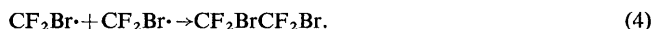
$$k_2/k_4^{\frac{1}{2}} \text{ (addition to } {=}CHF) = (1.2\pm0.3)\times10^2 \exp{(-3300\pm200/RT)},$$

$$k_2/k_4^{\frac{1}{2}} \text{ (addition to } {=}CF_2) = (2.0\pm0.3)\times10^2 \exp{(-4400\pm200/RT)},$$

$k_2/k_4^{\frac{1}{2}}$ (addition to ${=}CH_2$) = $(2.5\pm0.5) \exp{(-1000/RT)}$. A factors are in $l.^{\frac{1}{2}} mol^{-\frac{1}{2}} s^{-\frac{1}{2}}$; activation energies in kcal/mol; R = 1.99 cal deg.$^{-1}$ mol^{-1}; 1 cal = 4.184 J.

Absorption of light in the near u.-v. region, by a polyhalomethane normally leads to rupture of the weakest carbon-halogen bond and formation of the corresponding trihalomethyl radical and halogen atom.[1] With CCl_3Br, the excited state first formed, probably [1] (σ^*n), lives long enough to be collisionally deactivated.[2] Quantum yield measurements on the photolysis of CF_2Br_2 have shown that this molecule behaves in a similar way.[3]

In this paper we report the results of the photolysis of CF_2Br_2 in the gas phase with trifluoroethylene and ethylene. Arrhenius parameters for the rates of addition of difluorobromomethyl radicals to the olefins are derived from the temperature-variation data.

EXPERIMENTAL

MATERIALS

CF_2Br_2 obtained from Peninsular Chemresearch Inc. contained about 2 % of two impurities CF_2BrCF_2Br and CF_2HBr. These were removed by preparative G.L.C. using a 30 ft silicone oil column in a Pye Series 105 chromatograph. The resulting material was at least 99.7 % pure. Trifluoroethylene and ethylene were obtained from Cambrian Chemicals Ltd and were trap-to-trap distilled and degassed in the usual way. The dibromoethylenes were prepared by direct interaction of bromine (20 mm in 2 l.) with the appropriate olefin (22 mm in 2 l.) in the gas phase in the presence of daylight and then purified by preparative G.L.C. The 1,2-dibromotetrafluoroethane was commercial material used for identification purposes only.

METHOD

Materials were handled on a conventional vacuum line made of Pyrex. Unfiltered light from a Hanovia UVS 220 medium-pressure mercury arc was collimated by two quartz lenses and the nearly-parallel beam completely filled the cylindrical quartz reaction vessel (vol. 130 ml).

ANALYSIS

Reaction products were identified from their mass-spectra. A sample $(1.5\,\mu l.)$ of the reaction mixture was injected into a Perkin-Elmer F11 gas chromatograph fitted with a 100 m silicone oil capillary column. A fraction of the eluted material mixed with helium carrier was led, via a heated capillary leak, directly into the source of an A.E.I. Ltd. M.S. 12 mass spectrometer, and a mass spectrum was run on each component of the mixture as it emerged into the spectrometer source. Whenever possible the identification was confirmed by comparing the retention time with authentic material run under exactly the same conditions. Quantitative analysis was by G.L.C. on a Griffin and George D6 gas density balance chromatograph with a 6 ft column packed with 10 % silicone oil on 60-100 mesh Embacel.

RESULTS

The products of the photochemical reaction were identified from runs using mol ratios of CF_2Br_2 to olefin of 4 to 1; the runs lasted 2 h and the temperature was 150°. The products identified by mass spectrometry, together with the approximate mol percentages of each are shown in table 1. The difluorobromomethyl radical $CF_2Br\cdot$ is given the symbol X and the olefin E, so that CF_2Br_2 becomes XBr, CF_2BrCF_2Br becomes X_2. $CFHBrCF_2Br$ becomes EBr_2 etc.

TABLE 1.—PRODUCTS OF THE REACTION OF CF_2Br_2 WITH $CHF{=}CF_2$ AND $CH_2{=}CH_2$

symbol	$CF_2Br_2+CHF{=}CF_2$ compound	%	symbol	$CF_2Br_2+CH_2{=}CH_2$ compound	%
E	$CHF{=}CF_2$	—	E	$CH_2{=}CH_2$	—
XH	CHF_2Br	<1.0	XH	CHF_2Br	<1.0
XBr	CF_2Br_2 [a]	53.2	XBr	CF_2Br_2 [a]	83.6
X_2	CF_2BrCF_2Br [a]	9.3	X_2	CF_2BrCF_2Br [a]	1.4
EBr_2	$CF_2BrCHFBr$ [a]	15.1	EBr_2	CH_2BrCH_2Br [a]	13.2
XEBr	$CF_2BrCHFCF_2Br$	11.6	XEBr	$CF_2BrCH_2CH_2Br$	1.5
BrEX	CF_2BrCF_2CHFBr	6.1			
XEX	$CF_2BrCHFCF_2CF_2Br$	2.2			
$XE_2Br(1)$	$CF_2BrCHFCF_2CHFCH_2Br$	3.0			
(2)	$CF_2BrCHFCF_2CF_2CHFBr$ [b]	<1.0			
(3)	$CF_2BrCF_2CHFCHFCF_2Br$ [b]	<1.0			
(4)	$CF_2BrCF_2CHFCF_2CHFBr$ [b]	<1.0			

[a] identity confirmed from retention time; [b] identity assumed.

A series of experiments was carried out for each olefin in which the initial concentration of olefin [E] was varied, while the light intensity temperature and $[CF_2Br_2]$ remained constant. The amounts of each product formed, relative to the amount of CF_2Br_2 (which was always in excess, and remained virtually constant in any run since the overall percentage of reaction was kept small) are shown in tables 2 and 3.

In a second series of experiments, various concentrations, (again always excess) of CF_2Br_2 were photolyzed in the presence of a small constant amount of trifluoroethylene. The amounts of termination products formed, relative to CF_2Br_2 are shown in table 4.

TABLE 2.—VARIATION OF $CHF{=}CF_2$ CONCENTRATION

[CHF=CF₂] mol l.⁻¹ ×10⁴	[X₂]/[XBr] ×10²	[EBr₂]/[XBr] ×10²	[XEBr]/[XBr] ×10²	[BrEX]/[XBr] ×10²	[XEX]/[XBr] ×10²	[XE₂Br](1)/[XBr] ×10²	[XE₂Br](2)/[XBr] ×10²	[XE₂Br](3)/[XBr] ×10²	[XE₂Br](4)/[XBr] ×10²
33.8	0.268	7.05	10.4	8.13	1.51	3.66	1.45		
27.0	0.500	7.40	11.6	8.10	1.49	2.82	1.07	0.53	0.20
20.3	0.558	5.27	9.05	6.10	1.48	2.91	1.14	0.44	0.18
13.5	0.818	3.60	6.79	4.16	1.28	1.59			
10.1	0.984	3.26	6.09	3.44	1.15	1.09			
6.76	1.39	3.28	5.72	3.18	1.02	0.847			
3.38	2.24	3.69	5.18	2.45	0.755	0.359			
1.69	2.06	3.03	2.82	1.41	0.342	0.132			
0.68	1.49	1.85	0.72	0.34	0.059				

Initial $[CF_2Br_2] = 5.23 \times 10^{-3}$ mol l.⁻¹; photolysis time 1 h; temp. 140°C.

TABLE 3.—VARIATION OF $CH_2{=}CH_2$ CONCENTRATION

A [CH₂=CH₂] mol l.⁻¹×10⁴	[X₂]/[XBr] ×10²	[EBr₂]/[XBr] ×10²	[XEBr]/[XBr] ×10²	B [CH₂=CH₂] mol l.⁻¹×10⁴	[X₂]/[XBr] ×10²	[EBr₂]/[XBr] ×10²	[XEBr]/[XBr] ×10²
33.8	0.348	1.79	12.3	11.4	0.801	0.899	9.31
13.5	0.482	1.13	11.4	8.14	0.918	1.06	9.63
6.75	0.567	0.95	10.8	4.89	0.807	0.992	9.83
3.37	0.364	0.59	6.96	3.26	0.524	0.637	5.85
1.68	0.285	0.38	4.09	1.67	0.292	0.518	2.87

SERIES A: initial $[CF_2Br_2] = 4.97 \times 10^{-3}$ mol l.⁻¹; photolysis time 2 h at 165°C with Hanovia UVS 500 lamp.

SERIES B: initial $[CF_2Br_2] = 5.23 \times 10^{-3}$ mol l.⁻¹; photolysis time 1 h at 142°C with Hanovia UVS 220 lamp.

TABLE 4.—VARIATION OF CF_2Br_2 CONCENTRATION

[XBr] mol l.⁻¹×10³	[X₂]/[XBr] ×10²	[XEX]/[XBr] ×10²
18.3	0.987	0.248
15.7	1.25	0.292
13.1	1.46	0.323
10.4	1.59	0.409
7.85	2.54	0.677
5.86	2.79	0.725
5.23	2.87	0.961
3.25	—	1.56
2.62	4.75	1.61
1.97	6.22	1.84

Initial $[CF_2{=}CHF] = 0.327 \times 10^{-3}$ mol l.⁻¹; photolysis for 1 h at 130°C.

A series of photolyses was carried out for each olefin, using a large excess of CF_2Br_2. For each run the light intensity and reaction time were constant, but the temperature was different. The results are shown graphically in the form of Arrhenius plots in fig. 1 where $\log (R_{XEBr}/R_{X_2}^{\frac{1}{2}})$ has been plotted against reciprocal temperature.
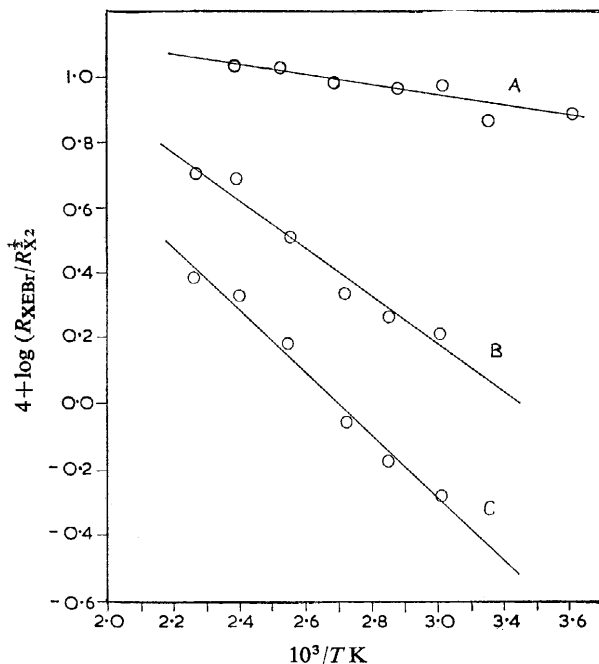
FIG. 1.—Arrhenius plots of log $(R_{\text{XEBr}}/R_{\text{X}_2}^{\frac{1}{2}})$ against $10^3/T$ K for ethylene and trifluoroethylene. Line A: addition to $=CH_2$; initial $[CH_2=CH_2] = 1.4 \times 10^{-3}$ mol l.$^{-1}$; initial $[CF_2Br_2] = 5.2 \times 10^{-3}$ mol l.$^{-1}$; time of photolysis 60 min. Line B: addition to $=CHF$. Line C: addition to $=CF_2$; initial $[CHF=CF_2] = 0.20 \times 10^{-3}$ mol l.$^{-1}$; initial $[CF_2Br_2]$ 5.3×10^{-3} mol l.$^{-1}$; time of photolysis 15 min.

DISCUSSION

Two initiation processes in the photolysis of CF_2Br_2 have been observed. In solution, homolytic fission of the carbon-bromine bond leads to difluorobromomethyl radicals and bromine atoms.[4, 5]   Flash photolysis of CF_2Br_2 leads to the formation of difluoro carbene.[6, 7]

$$CF_2Br_2 + h\nu \rightarrow CF_2Br\cdot + Br\cdot \tag{1}$$

$$CF_2Br_2 + h\nu \rightarrow CF_2 : + Br_2. \tag{1'}$$
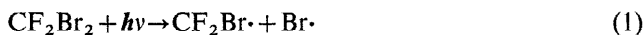
All the products of the photochemical reactions can be simply related to the reactions of difluorobromomethyl radicals and bromine atoms formed in (1); no tetrafluoro-ethylene, formed by dimerization of CF_2: was found in any run, and no cyclopropenes formed by addition of CF_2: to the olefins were detected.   In a separate gas-phase photolysis, equal amounts of CF_2Br_2 and cyclohexene were reacted together.   Cyclo-

hexene is known[8] to trap CF_2: as the difluoronorcarane F_2C⟨⬡⟩.   Coupled

G.L.C. + mass-spectral analysis of the products showed no difluoronorcarane, no tetrafluoroethylene and no other products not attributable to $CF_2Br\cdot$ or $Br\cdot$ reactions. Under the conditions of these photolyses, and with the medium pressure mercury arc, therefore, only homolytic fission to give difluorobromomethyl radicals (1) occurs to an appreciable extent and (1') can be eliminated.

Difluorobromomethane (XH) was observed in trace amounts only, too small for

quantitative analysis, and probably represents hydrogen abstraction from the products by $CF_2Br\cdot$ radicals. Addition of difluorobromomethyl radicals to the olefin (2) and (3) produces the adduct by the usual chain process:

$$X\cdot + E \rightarrow XE\cdot \qquad (2)$$

$$XE\cdot + XBr \rightarrow XEBr + X\cdot \qquad (3)$$

Both possible adducts (XEBr and BrEX), formed by addition of $CF_2Br\cdot$ to either end of trifluoroethylene were found. The products X_2 and XEX can be attributed to radical-radical termination reactions, and the dibromides EBr_2 are probably formed by addition of Br_2 to unused olefin in the liquid phase when the products are condensed for analysis.

Tables 2 and 3 shows that a simple chain mechanism, of the kind proposed for the photochemical addition of CCl_3Br to fluoro-olefins,[9] is inadequate in this case. Although the CF_2Br_2 was always in excess, the dibromide/dimer ratio $[EBr_2]/[X_2]$ is not equal to one, and the cross-combination product XEX becomes the main termination product at low olefin concentrations. The rate of adduct (XEBr) formation is not proportional to the olefin concentration, except at the lowest values, and no simple power law relates the rate of formation of any product to the olefin concentration.
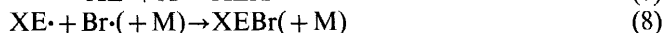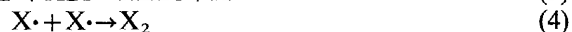
<div align="center">MECHANISM</div>

Excited CF_2Br_2 molecules are formed in the first step of the photolysis. These can be collisionally deactivated,[3] or they can decompose. The rate of decomposition of the CF_2Br_2 is given by [2]

$$I_a \left[1 - (1 - \phi_\infty) \prod_{i=1}^{n} (1/(1 + P_i/M)) \right],$$

where I_a is the absorbed light intensity, P_i is the ratio of the rate constant for decomposition to the rate constant for deactivation, M represents the total concentration of molecules able to deactivate the excited CF_2Br_2 and ϕ_∞ is the quantum yield of decomposition at infinite concentration of M.

The following reactions need to be included:

$$XBr + h\nu \rightarrow X\cdot + Br\cdot \qquad (1)$$
$$X\cdot + E \rightarrow XE\cdot \qquad (2)$$
$$XE\cdot + XBr \rightarrow XEBr + X\cdot \qquad (3)$$
$$X\cdot + X\cdot \rightarrow X_2 \qquad (4)$$
$$X\cdot + Br\cdot(+M) \rightarrow XBr(+M) \qquad (5)$$
$$Br\cdot + Br\cdot + M \rightarrow Br_2 + M \qquad (6)$$
$$XE\cdot + X\cdot \rightarrow XEX \qquad (7)$$
$$XE\cdot + Br\cdot(+M) \rightarrow XEBr(+M) \qquad (8)$$

This mechanism differs from the simple case,[9] in the inclusion of four extra terminations.

The three termination steps (4), (5) and (6) are clearly important at all olefin concentrations, and the cross combination reaction (7) becomes important as the olefin concentration increases. In view of the initially equal concentrations of $X\cdot$ radicals and $Br\cdot$ atoms there seems little doubt that the cross-combination (8) should also be included, the product of which is identical with the adduct. The additional termination (9),

$$XE\cdot + XE\cdot \rightarrow XE_2X \qquad (9)$$

involving dimerization of the $XE\cdot$ radicals can be neglected since none of the product XE_2X was detected. It undoubtedly becomes important at higher olefin concentrations, however.

Exact solution of the steady-state equations is difficult since there are five termination steps. If, however, it is assumed that $k_7[X\cdot] \ll k_3[XBr]$, which seems justified for this concentration range, an expression of manageable form is obtained for the rate of dimer (CF_2BrCF_2Br) formation.

$$R_{X_2} = I_a\left[1-(1-\phi_\infty)\prod_{i=1}^{n}\frac{1}{(1+P_i/M)}\right]\bigg/\left[2+2\frac{k_2k_7[E]}{k_3k_4[XBr]}+\left(\frac{k_5M^{\frac{1}{2}}}{(k_4k_6)^{\frac{1}{2}}}\right)\times\right.$$
$$\left.\left(1+\frac{k_2k_7[E]}{k_3k_4[XBr]}\right)^{\frac{1}{2}}\left(1+\frac{k_2k_8[E]}{k_3k_5[XBr]}\right)\right], \qquad \text{(A)}$$

where R_{X_2} is the rate of dimer formation, and $R_{X_2} = R_{Br_2}$. The rate of cross combination product formation R_{XEX} is given by

$$R_{XEX} = \frac{k_2k_7[E]}{k_3k_4[XBr]}R_{X_2}. \qquad \text{(B)}$$

The value of ϕ_∞, the quantum yield at infinite pressure, is very small for CF_2Br_2 [3] and ϕ_∞ may be neglected. If we make the further approximation that the cascade deactivation, represented by the product over all the vibrational levels (π) in (A) can be replaced by a single-stage deactivation, i.e., the " strong deactivation " assumption, then the numerator of (A) can be considerably simplified. There are three rate constant ratios in the denominator of (A); we define $\alpha = k_2k_7/k_3k_4$ and $\beta = k_5/(k_4k_6)^{\frac{1}{2}}$. The ratio of the two radical-radical combinations k_7/k_4 is certainly close to one, since radical combinations in the gas phase occur at nearly every collision. Similarly, the ratio of the two atom-radical combinations k_8/k_5 will be close to one. We assume therefore that $k_7/k_4 = 1 = k_8/k_5$, and hence $k_2k_7/k_3k_4 = \alpha = k_2k_8/k_3k_5$.

The absorbed light intensity I_a is given by

$$I_a = 2.30\, I_0\, \varepsilon\, 1[XBr] = \theta[XBr]$$

(and θ is constant in any series of experiments where I_0 is constant) since the extinction coefficient ε is small in the near u.-v. Incorporating all these simplifications, eqn (A) and (B) become

$$\frac{R_{X_2}}{\theta[XBr]} = \left(\frac{P}{(P+M)}\right)\bigg/\left(1+\frac{\alpha[E]}{[XBr]}\right)\left[2+\beta M^{\frac{1}{2}}\left(1+\frac{\alpha[E]}{[XBr]}\right)^{\frac{1}{2}}\right], \qquad \text{(C)}$$

and

$$R_{XEX} = \alpha([E]/[XBr])R_{X_2}, \qquad \text{(D)}$$

where $R_{X_2}/\theta[XBr]$ is the quantum yield of dimer formation. In deriving (C) and (D) it has been assumed that the atom-radical combinations (5) and (8) are termolecular; if, however, these reactions are in the bimolecular region then the term $\beta M^{\frac{1}{2}}$ in eqn (C) should be replaced by $\beta/M^{\frac{1}{2}}$.

When the rate of dimer formation equals the rate of cross-combination product formation, i.e., $R_{X_2} = R_{XEX}$, then from (D) $\alpha = [XBr]/[E]$. Interpolation of the results in table 2 gives the concentration of olefin at which the rates are equal, and $\alpha = 5.88$ (140°). The cross-combination rate constant ratios for small free radicals are found experimentally,[10] and predicted from collision theory to be about 2 in the gas phase. Experimental evidence for the same rate constant ratio with atom-radical combinations, e.g., β is lacking. The recombination rate constant for $CF_2Cl\cdot$

radicals is known [11] and k_4 the recombination rate constant for $CF_2Br\cdot$ is probably of the same order of magnitude, viz., about 10^{10} l. mol^{-1} s^{-1}. The termolecular combination rate constant for bromine atoms k_6 is about 10^9 l.^{2} mol^{-2} s^{-1} for several different third bodies.[12] The cross-combination rate constant k_5 for $CF_2Br\cdot$ and $Br\cdot$ is probably intermediate between the two values of 10^{10} and 10^9, so that a value of $\beta = 2 = k_5/(k_4/k_6)^{\frac{1}{2}}$ would seem to be appropriate. The decomposition-deactivation rate constant ratio P for CF_2Br_2 is [2, 3] about 10^{-4} mol l.$^{-1}$. The only unknown in eqn (C) is θ, so that a comparison of the experimental results, with the predictions of
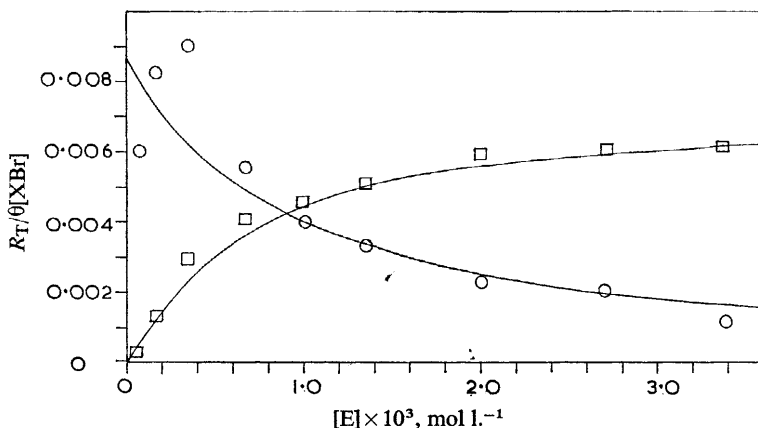

FIG. 2.—Comparison of experimental and calculated rates of product formation at various olefin concentrations. Circles $R_T = R_{X_2}$; squares $R_T = R_{XEX}$; full lines calculated from eqn (C) and (D).

eqn (C) can be made by varying θ to give the best fit. Such a comparison is shown in fig. 2 where the solid line was calculated taking $\alpha = 5.88$, $\beta = 2.0$, $P = 10^{-4}$ mol l.$^{-1}$, and the individual points are the experimental results from table 2 divided by the appropriate value of θ which was 6.9×10^{-4}. $CF_2{=}CHF$ is probably less effective in deactivating the excited molecules than the parent CF_2Br_2 and the olefin contribution to M has been neglected, although since CF_2Br_2 was always in considerable excess the numerator of eqn (C) is almost constant and the calculation is dominated by changes in the denominator. The same calculation can be made using the form of (C) appropriate for bimolecular atom-radical combination (5), i.e., with $\beta M^{\frac{1}{2}}$ replaced by $\beta/M^{\frac{1}{2}}$. With this form of the equation good agreement between experiment and calculation cannot be obtained for any value of θ, unless a very small cross-combination ratio β (<0.1) is accepted. Such a value of β seems unlikely and we conclude that (5) is termolecular over the pressure range here studied.

The results of the second series of experiments (table 4), where the concentration of CF_2Br_2 was varied, are also in agreement with the predictions of eqn (C) and (D). Since the CF_2Br_2 was in excess, the concentration M of third body now varies and a completely different form of curve is generated. In making the calculation the same values of α, β and P were used, but the experimental points have been fitted to the calculated curve by using $\theta = 12.4 \times 10^{-4}$. This larger value of θ is expected since the optical systems used in the two sets of experiments were different. The comparison between experiment and calculation is shown in fig. 3.

In general, (C) predicts the experimental results quite well, although some discrepancies show up at the low-pressure end in both sets of results. The experimental results are least reliable at the low pressure end, since here heterogeneous processes are expected to become more important. The initial increase in the experimental

$R_{X_2}/\theta[XBr]$ shown in fig. 2 for trifluoroethylene appears to be real, and a similar effect occurred on increasing the olefin concentration when ethylene was used (see table 3). A possible cause of this initial increase is photosensitized decomposition of the CF_2Br_2 by the olefin. The behaviour of the system can be satisfactorily described by the mechanism proposed, the main difference from the simple case [9] being the termination process.
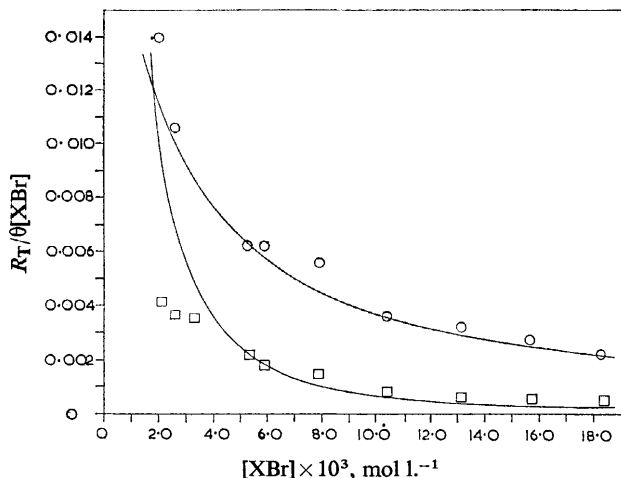

FIG. 3.—Comparison of experimental and calculated rates of product formation at various CF_2Br_2 concentrations. Circles $R_T = R_{X_2}$; squares $R_T = R_{XEX}$; full lines calculated from eqn (C) and (D).

The changes in the order of the reaction with respect to [E] are a consequence of the changing termination step. The atom-radical recombination step (5) appears to be termolecular. This result is not entirely unexpected since many atom-diatomic radical combinations are third order,[13] and the radical-radical combinations of methyl [14] and trifluoromethyl [15] also become third order at high temperatures. Also, in order to explain the second set of results with various CF_2Br_2 pressures the existence of an excited state of sufficiently long life to undergo collisional deactivation must be invoked.

The pressure-variation data for ethylene could also be interpreted in terms of eqn (C). We were unable to detect the cross-combination product $XEX(CF_2BrCH_2$ $CH_2CF_2Br)$ in this case, although the fact that the amounts of dimer X_2 and di-bromide EBr_2 formed are not equal (see table 3) indicates that the cross-combination must have occurred. The involatility of this product may have broadened the peak too much for observation in the G.L.C. analysis. In view of this lack of data, no attempt has been made to match the experimental results with those calculated from (C). A value for α of about 2.5 would seem to fit the data in table 3 best. α is effectively k_2/k_3, since $k_7/k_4 \approx 1$. The rate constant k_2 for addition of X· to trifluoro-ethylene, is expected to be less than the rate constant for addition to ethylene, so that the lower value of α found for ethylene indicates a lower reactivity for the XCH_2—$\dot{C}H_2$ radical in comparison with $XCHF$—$\dot{C}F_2$ which is in agreement with expectation.

The rate of adduct formation R_{XEBr} is a complex function of the reactant concentrations. However, from the mechanism, provided (8) the combination of XE· with Br· is negligible.

$$R_{XEBr}/R_{X_2}^{\frac{1}{2}} = k_2[E]/k_4^{\frac{1}{2}}.$$

In the final series of experiments (fig. 3) a large constant excess of CF_2Br_2 was used with each olefin in turn to minimize contributions from (8). Least-squares treatment of the data yielded the following Arrhenius constants.
For addition to $=CHF$ of trifluoroethylene:

$$k_2/k_4^{\frac{1}{2}} = (1.2 \pm 0.3) \times 10^2 \exp(-3300 \pm 200/RT),\ \text{l.}^{\frac{1}{2}}\ \text{mol}^{-\frac{1}{2}}\ \text{s}^{-\frac{1}{2}}.$$

For addition to $=CF_2$ of trifluoroethylene:

$$k_2/k_4^{\frac{1}{2}} = (2.0 \pm 0.3) \times 10^2 \exp(-4400 \pm 200/RT),\ \text{l.}^{\frac{1}{2}}\ \text{mol}^{-\frac{1}{2}}\ \text{s}^{-\frac{1}{2}}.$$

For addition to $=CH_2$ of ethylene:

$$k_2/k_4^{\frac{1}{2}} = (2.5 \pm 0.5) \exp(-1000 \pm 500/RT)\ \text{l.}^{\frac{1}{2}}\ \text{mol}^{-\frac{1}{2}}\ \text{s}^{-\frac{1}{2}}.$$

If we assume that for combination of $CF_2Br\cdot$ radicals $A_4 = 10^{10}$ l. $\text{mol}^{-1}\ \text{s}^{-1}$, $E_4 = 0$, then absolute Arrhenius parameters for addition of $CF_2Br\cdot$ radicals to the olefins can be found. These are shown, together with some known values for other radicals in table 5.

TABLE 5.—ARRHENIUS PARAMETERS FOR THE ADDITION OF VARIOUS RADICALS TO FLUORO-ETHYLENES

site radical	$=CH_2$[a]		$=CHF$[b]		$=CF_2$[c]		
	E_2	log A_2	E_2	log A_2	E_2	log A_2	ref.
$CF_2Br\cdot$	1.0	5.3	3.3	7.0	4.0	7.3	this work
$CCl_3\cdot$	3.2	6.5	6.1	7.2	7.1	7.3	9
$SF_5\cdot$	1.9	5.6	3.4	6.4			16
$CH_3\cdot$	6.8	8.1					17
$C_2H_5\cdot$	5.5	7.3					18
$C_3H_7\cdot$	5.1	8.4					17

[a] $=CH_2$ in ethylene; [b] $=CHF$ in trifluoroethylene; [c] $=CF_2$ in trifluoroethylene.

When CF_2Br_2 adds to trifluoroethylene in the gas phase the ratio of the amounts of the two isomeric 1 to 1 adducts formed is 2.38 at 100°. Coscia found this ratio to be 2.4 (at 100°) when CF_2Br_2 adds to the olefin in the liquid phase,[5] so that the selectivity of the radical differs little in the gas and liquid phases. Similarly, when CCl_3Br adds to trifluoroethylene,[9] the ratio in the gas phase at 100° is 3.7, so that $CF_2Br\cdot$ radicals are more reactive and less selective than CCl_3 radicals in the gas phase.

The rates of addition of $CF_2Br\cdot$ radicals show the same trends as CCl_3 radicals, and the electrophilic character of the radical plays an important part in determining its reactivity. The results lend further support to the idea that the rate of addition of a polar radical is not controlled by a single factor such as the stability of the addend radical. In the same way that the correlation between reactivity of polar CCl_3 radicals towards polar substrates with localization energy, calculated from M.O. theory, is only moderate,[9] from the three results available with $CF_2Br\cdot$ radicals the same is true here. Electrostatic interactions undoubtedly play an important part in the formation of the transition state.

At high olefin concentrations measurable amounts of 2-to-1 telomers were formed. The experiments reported in table 2 were performed at 140°, where the ratio of the two 1-to-1 isomeric adducts is 1.45. There are four 2-to-1 telomers and the first two, (no. (1) and (2) in table 2) are probably formed by addition of $CF_2BrCHFCF_2$ radicals to trifluoroethylene, and the ratio of the telomers is 2.6. The second two (no. (3) and (4) in table 2) are probably formed by addition of $CF_2BrCF_2CHF\cdot$ radicals to trifluoroethylene, and the ratio of the telomers is also 2.6. At 140° the ratio of

isomers formed by CCl_3 addition [9] is 3.3. The order of reactivity is $CF_2Br\cdot >$ $CF_2BrCHFCF_2\cdot \approx CF_2BrCF_2CHF\cdot > CCl_3\cdot$ in agreement with the reactivity order expected from the increasing electrophilic character going from $CCl_3\cdot$ to $CF_2Br\cdot$.

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