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Kinetics of Addition of CF₃ Radicals to Olefins and their Derivatives

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The photolysis of hexafluoroazomethane was investigated in iso-octane solution at 65°. It was shown that CF₁H, C₂F₈ and N₂ are the only products of the photolysis, if the azo-compound concentration is kept below 10^{-2} M and the rate of decomposition is less than 1%/6/hour. The ratios CF₁H/N₂ and C₂F₈/N₂ are constant and independent of concentration in the range $1.6 \times 10^{-3} - 40 \times 10^{-3}$ M, and their sum (CF₁H + 2C₂F₆/N₂ are constant and independent of concentration in the range $1.6 \times 10^{-3} - 40 \times 10^{-3}$ M, and their sum (CF₁H + 2C₂F₆/N₂ is unaffected. Hence, the effect of the concentration and of the added substrates indicates that all the C₂F₆ results from a "cage" recombination. The decrease in the CF₁H/N₂ ratio, arising from the addition of suitable substrates, is attributed to the addition reaction CF₃ + substrate \rightarrow substrate CF_3 , (k₂) which competes with the abstraction reaction CF₄ + iso-octane \rightarrow CF₃H + iso-octyl radical, (k₁) for CF₃ radicals. From the decrease in the CF₃H/N₂ ratio, values of k_2/k_1 have been calculated, and these confirm the proposed mechanism. The following values were obtained for k_2/k_1 : C₂H₄- 2×225 ; CH₃·CH:CH₂--630; (CH₃)₂·C:CH₂--1720; C₂H₅·CH:CH₂--653; iso-C₃H₇·CH:CH₂--704; t-C₄H₉·CH:CH₂--653; cis-CH₃·CH:CH₄- -2×290 ; trans-CH₃·CH:CH:CH₃- -2×292 ; CH₂:C:CH₂--290; CH₃·CH:C:CH·CH₃--412; CH=CH- -2×62.5 and CF₂:CF₂- 2×34.3 . These values are all greater than the respective methyl affinities, but C₂F₄ is less reactive than C₂H₄ with regard to CF₄ addition, whereas for CH₃ addition it is 10 times more reactive. These results show the strongly electrophilic character of CF₄ radical.

Extensive studies of the addition of methyl radicals to various aromatic, olefinic and acetylenic compounds have been carried out in this Laboratory.¹ The results accumulated in the course of these investigations show how the rate constants of addition depend upon the atom localization energy of the substrate and the steric hindrance caused by the presence of bulky substituents attached to the reaction center. A quantitative treatment of these effects has been outlined in recent papers by Szwarc and Binks.²

The effect of polar groups upon the rate of addition also has been studied.³⁻⁵ It appears that in the addition process the methyl radical behaves as if it were a slightly nucleophilic reagent—the rate of the reaction being enhanced by such substituents as Cl or Br and reduced by OCH₃ or N(CH₃)₂. It was felt, however, that the effect of polarity deserves more intensive study and that investigations involving some highly polar radical would be particularly advisable. After some considerations, we chose for this purpose the trifluoro methyl radical as its polarity is very high and its complexity resembles that of a methyl radical.

A method which permits us to study the rate of addition of CF₃ radicals to a variety of substrates was eventually developed. This is described in the present paper. In addition, we also report our findings concerning the addition of CF₃ radicals to some olefins and their halogen derivatives. These data show clearly the strong electrophilic character of CF₃ radicals. It is hoped that the continuation of this work will provide much data of value in

(1) (a) M. Levy and M. Szware, J. Am. Chem. Soc., 77, 1949 (1955);
 (b) R. P. Buckley and M. Szware, Proc. Roy. Soc. (London), A240, 396 (1957);
 (c) M. Gazith and M. Szware, J. Am. Chem. Soc., 79, 3359 (1957);
 (d) A. Rajbenbach and M. Szware, Proc. Roy. Soc., (London), A251, 1266 (1959), and other papers.

(2) (a) M. Szwarc and J. H. Binks, Kekule Symposium, London, 1958, published in "Theoretical Organic Chemistry," Butterworth Publ., 1959, p. 262; (b) J. H. Binks and M. Szwarc, J. Chem. Phys., 30, 1494 (1959).

(3) R. P. Buckley and M. Szwarc, J. Am. Chem. Soc., 78, 5696 (1956).

(4) R. P. Buckley, A. Rembaum and M. Szwarc, J. Chem. Soc., 3442 (1958).

(5) J. Gresser, J. H. Binks and M. Szwarc, J. Am. Chem. Soc., 81, 5004 (1959).

developing a more quantitative treatment of the effect of polarity upon the rates of radical addition.

Generation of CF_3 Radicals and their Modes of Reaction with the Solvent.—Trifluoromethyl radicals were generated by photolysis of hexafluoroazomethane which was prepared by the action of IF₅ on cyanogen iodide according to the method described by Dacey.⁶ The crude hexafluoroazomethane was purified by passing it through towers containing alkali and drying agent and then by low temperature distillation. The purified material was stored in a blackened glass bulb and its purity checked by vapor phase chromatography which showed the absence of any other substances.

The photolysis was carried out in iso-octane solution. The spectroscopically pure solvent, acquired commercially, was further purified by passing it through an active silica column to remove traces of unsaturation and then carefully frac-tionated. The azo-compound and the purified and deaerated solvent were condensed into special glass ampoules (each 10 cc. of volume) which were then sealed under vacuum. The sealed ampoules were immersed in a constant temperature bath and irradiated by means of a high pressure mercury lamp (G.E.AH-6). The irradiation was continued for 7-18 hr., during which period not more than 10% of the azo-compound was decomposed. The irradiated ampoules were cooled to room temperature, opened under high-vacuum and the gaseous products collected on a high vacuum line. The details of the procedure concerned with filling the ampoules and collecting the gaseous products have been described elsewhere^{1c,7} and hence will not be repeated in this paper.

The photolysis produced three gaseous products, namely, CF₃H, C₂F₆ and N₂. These, as well as the undecomposed hexafluoroazomethane, were transferred by a toepler pump into a 1 liter storage flask equipped with an internal polyethylene fan magnetically driven. The mixing of the collected gases was found to be essential to insure the uniformity of the aliquots withdrawn from the storage flask for gas-chromatographic analyses, and the intro-

(6) J. R. Dacey and D. M. Young, J. Chem. Phys., 23, 1302 (1955).
(7) C. Steel and M. Szwarc, *ibid.*, 33, 1677 (1960).

duction of the fan improved greatly the reproducibility and precision of the results. The aliquots were analyzed on a special gas-chromatographic unit with a silica gel column, the unit being permanently attached to the system.

To calibrate the gas-chromatogram standard mixtures of CF₃H, $C_{2}F_{6}$ and nitrogen were analyzed. Samples of the fluoro-carbons were kindly supplied by the Research Department of Du Pont Co., and their purity was checked by mass-spectro-graphic analysis. Two methods were used in determining the proportion of the gases formed. In the first method the height of each peak was measured and the result was converted into mmoles of the respective component by using a suitable calibration curve. For a rigorously standardized gaschromatographic procedure, the height of the peak was found to be a more satisfactory measure of the amount of the analyzed gas than the area under the curve. In the second analytical method the ratios of the peak heights corresponding to CF₃H and N₂ and to C_2F_6 and N_2 were measured, and it was found that such ratios were strictly proportional to the molar ratios of the respective components. This proportionality was maintained even in those cases when the peak heights were not exactly proportional to the amounts of the components. The first method of analysis was used in the earlier experiments, and it was essential in determining the material balance of the products of the reaction. The second method was found to be quicker and even more reliable whenever the *relative* molar ratios such as $CF_{2}H/N_{2}$ and $C_{2}F_{6}/N_{2}$ were required. As the relative ratios are sufficient for calculating the relative rate constants of addition of CF_3 radicals (see the following section), the latter method was used in most of the experiments.

Photolysis of hexafluoroazomethane in iso-octane solution was investigated at 65° at three different concentrations of the azo-compound, namely, 1.5 $\times 10^{-8}$, 8 $\times 10^{-3}$ and 40 $\times 10^{-3}$ M. The results which are given in Table I show that within

TABLE I

The Material Balance of the Products of Hexafluoroazomethane Photolysis in Iso-octane Solution. $T = 65^{\circ}$

		-	-	
$ \begin{array}{c} [\mathrm{CF}_{1}\cdot\mathrm{N}_{2}\cdot\mathrm{CF}_{1}] \\ M \times 10^{3} \end{array} $	Time of photoly- sis, hr.	$\frac{CF_{2}H}{N_{2}}$	2C2F6 N2	$\frac{CF_{2}H + 2C_{2}F_{6}}{N_{2}}$
1.5	29	1.44	0.555	2.00
1.5	29	1.45	.555	2.00
1.5	29	1.45	.580	2.03
1.5	29	1.45	.570	2.02
1.5	29	1.43	.550	1.98
8	16	1.44	.550	1.99
8	16	1.45	.565	2.01
8	16	1.42	.575	1.99
8	8	1.45	.547	1.995
8	8	1.45	.561	2.01
40	4	1.44	.495	1.935
40	4	1.49	. 550	2.04
40	4	1.44	.535	1.975
40	4	1.45	. 535	1.985

the investigated range of concentration the ratio of the products remained constant. Moreover, these results show that *all* the trifluoromethyl radicals formed by the photolysis were found either as $CF_{8}H$ or as $C_{2}F_{6}$. This means that under our experimental conditions all the radicals which escaped the "cage" recombination reacted with the solvent according to

 CF_{8} + iso-octane \longrightarrow $CF_{8}H$ + iso-octyl radical (1) and none recombined with solvent radicals.

The hexafluoro-ethane must result entirely from a "cage" recombination, since a 25-fold variation in the azo-compound concentration did not affect the C_2F_0/N_2 ratio. Experiments carried out in the presence of a suitable scavenger for CF₃ radicals, such as isobutene, provide further evidence for the lack of a bimolecular recombination. As seen in Table II, increasing amounts of isobutene added to the CF₃N₂CF₃-iso-octane solution greatly reduced the CF₃H/N₂ ratio but left the 2C₂F₆/N₂ ratio unchanged. Similar results were obtained with other substrates.

Only $\sim 25\%$ of CF₂ radicals recombine in a "cage" under our experimental conditions. On the other hand, about 70% of CH₃ radicals formed in photolysis of azomethane recombine under the same conditions (65°, iso-octene solvent). This might imply higher activation energy for CF₃ recombination than for CH₃ recombination.

TABLE 11									
T_{HE}	Effect	OF	Added	ISO-BUTENE	ON	THE	PHOTOL	YSIS	OF
				CF ₃ ·N ₂ ·CF ₃					

Solvent	iso-octane:	T	=	659
Solvenc,	150°°°Ctanc,	-	_	00

Mole % of iso-butene	CF:H/N2	2(C2F4)/N2	k1/k1
0.000	1.447	0.547	••
.000	1.443	.558	••
.000	1.451	.561	••
.0492	0.787	.533	1704
.1002	. 530	.535	1714
.262	.259	.542	1747
.657	.183	.558	
.773	.092	.540	1908 (?)
.000	1.465 ^a	$.492^{a}$	••
.047	0.848°	.475°	1784
.097	.608*	,49 2ª	1655
.131	. 503°	.480*	1573
.165	.416ª	.472ª	1700
.210	,351°	.490°	1693

^a These are older results in which the absolute calibration was not yet improved.

Our results differ from those obtained by Dacey and Young.6 Those workers photolyzed gaseous hexafluoro-azomethane in the absence of any diluent. They found that under their conditions CF3 radicals may dimerize or add to the undecomposed azo-compound, the latter reaction producing $(CF_3)_{2}$ - $N \cdot N(CF_3)_2$ or $[(CF_3)_2N \cdot N(CF_3)]_2$. The fraction of the addition product increased with increasing pressure of the hexafluoro-azomethane, being negligible for pressures less than 1 mm., increasing to about 15% at 10 mm. and to about 40% at 100 mm. Since our studies were carried out at very low concentration of the azo-compound $(10^{-2} 10^{-3}$ M) and in the presence of a large excess (10^{3} -104) of a solvent (iso-octane) which competes with the azo-compound for the CF₃ radicals, the addition reaction observed by Dacey and Young had to be of no importance in our system.

Determination of the Relative Rate Constants of CF_3 Radical Addition.—It was shown in the preceding section that all the CF_3 radicals generated in the photolysis either abstract hydrogen atoms from the solvent and form CF_3H

$$CF_3 + iso-octane \longrightarrow CF_3H + iso-octyl radical (1)$$

or undergo a "cage" recombination which converts a *constant* fraction of the CF₆ radicals into C_5F_6 . The magnitude of this fraction depends upon the temperature of the reaction and the nature of the solvent but is independent of the concentration of the azo-compound, the intensity of the actinic light or the presence of substrates added in small quantities to the solution.

The decrease in the CF_3H/N_2 ratio resulting from the presence of a suitable substrate A is due to the reaction

$$CF_* + A \longrightarrow A \cdot CF_3$$
 (2)

In view of the low stationary concentration of all the radicals present in the system, the recombination of CF_3 radicals with A CF_3 is of no importance. As shown in the preceding section, CF3 radicals do not recombine with isoöctyl radicals; addition of a reactive substrate reduces the stationary concentration of CF_3 , making the A CF_3 recombination even less likely. Thus, in the photolysis carried out in a mixture of iso-octane and a suitable substrate A, those CF₃ radicals which have diffused into the solvent undergo only reaction 1 or 2. The kinetic approach developed for studies of methyl radical addition¹ may therefore be applied to the present problem. If we denote by (CF_3H) N_2)_f the fraction of CF₃ radicals reacting with the solvent according to equation 1 and by $CF_3 \cdot A/N_2$ that fraction reacting with A according to equation 2, then

$$(CF_3 \cdot A/N_2)/(CF_3H/N_2)_f = (k_2/k_1)(X_A/X_B)$$

where X_A and X_S denote the respective mole fractions of the substrate A and the solvent in the reacting mixture. In view of the established products' balance, (CF₃A/N₂) may be found from the equation

$$(CF_3 \cdot A/N_2) = (CF_3H/N_2)_b - (CF_3H/N_2)_i$$

where $(CF_3H/N_2)_b$ represents the respective product ratio in a "blank," *i.e.* in an experiment performed in the absence of A. It follows, therefore, that

$$k_2/k_1 = \{ [(CF_3H/N_2)_b - (CF_3H/N_2)_f] / (CF_3H/N_2)_f \} (X_S/X_A) \}$$

Variation of the mole ratio X_S/X_A left k_2/k_1 unchanged (see Table II), thus verifying the proposed mechanism. Similar results were obtained with other substrates (see Table III).

It was shown in one series of experiments that k_2/k_1 (for butene-2) is independent of $[CF_3N_2CF_3]$. The latter was changed from 2.8 \times 10⁻⁵ M to 12.4 \times 10⁻⁵ M.

Our treatment involves the assumption that only the addition of CF_3 radicals to the substrate takes place in the process. However, in some cases abstraction of an H atom from the substrate may also occur as shown by

$$CF_3 + A \longrightarrow CF_3H + (A-H) \text{ (olefin)}$$
 (3)

Such a situation was considered in reference 1c,

TABLE III

Relative	RATES	of A	DDITION	OF C	CF ₈ I	RADICALS	(k_2)	ΑT
65° Giver	N IN THE	Form	t of k_2/k	wни	ere k	a Refers	то т	HE
F	EACTION	V CF3	$+ C_8 H_{18}$	→ C	$F_{3}H$	$+ C_{8}H_{17}$		

Substrate	Range of conc. in mole fraction × 10 ³	No. of expts.	k2/k1			
C ₂ H ₄ (I series)	1.5-7.0	5	452 ± 12			
C_2H_4 (II series)	0.6-2.0	4	447 ± 31			
C_2H_4 (III series)	1.0-4.0	$\overline{5}$	468 ± 35			
$CH_3CH = CH_2$ (I series)	1.0-4.0	5	610 ± 39			
CH ₃ CH==CH ₂ (II series)	1.0-4.0	5	633 ± 9			
$(CH_3)_2C = CH_2$ (I series)	0.5 - 2.0	5	1681 ± 75			
$(CH_3)_2C = CH_2$ (II						
series)	.5-2.0	5	1642 ± 44			
$(CH_3)_2C = CH_2$ (III						
series)	.5-10.0	5	1721 ± 23^{a}			
$C_2H_5 \cdot CH = CH_2$.6 - 2.6	6	687 extrp. to 0%			
$iso-C_3H_7\cdot CH = CH_2$.7-2.8	5	$704\mathrm{extrp.}\mathrm{to}0\%$			
$t-C_4H_9 \cdot CH = CH_2$	2.0 - 10.0	6	658 ± 11			
cis-CH ₃ ·CH=CH·CH ₃	0.5-3.0	12	$580 \mathrm{extrp.} \mathrm{to} 0\%$			
trans-CH ₃ ·CH==CH·CH ₃	0.6-3.0	6	$585\mathrm{extrp}$, to 0%			
$CH_2 = C = CH_2 (I \text{ series})$	1.2 - 4.2	5	299 ± 9			
$CH_2 = C = CH_2$ (II						
series)	1.1 - 5.0	4	283 ± 20			
CH ₃ ·CH=C=CH·CH ₃	1.6 - 5.0	8	413 extrp. to 0%			
CH≡CH	0.7-3.0	5	125 ± 8			
C_2F_4	3.2 - 11.5	6	68.6 ± 4.2			
^{<i>a</i>} This we believe is the most reliable value.						

and the treatment developed there is applicable to the present system. It was shown that under these conditions the entity

$$\{(CF_{3}H/N_{2})_{f}/[(CF_{3}H/N_{2})_{b} - (CF_{3}H/N_{2})_{f}]\}(X_{A}/X_{S})$$

varies linearly with X_A/X_S , the intercept of the resulting straight line giving k_1/k_2 while its slope represents k_3/k_2 . Such situations were encountered when substrates such as butene-1 or butene-2 were investigated.

Finally, it should be emphasized that the calculation of k_2/k_1 or k_3/k_2 does not require knowledge of the *absolute* ratios of CF₃H/N₂ but only their *relative* values. Hence, the second technique, discussed in the preceding section, is sufficient to provide all the data necessary for the calculation of the relative rate constants of CF₃ radical addition.

Results

In the course of this work the relative rate constants of CF₃ addition to the following substrates were determined: ethylene, propylene, iso-butene, butene-1, isopropylethylene, *t*-butylethylene, *cis*butene-2, *trans*-butene-2, allene, 2,3-pentadiene, acetylene and tetrafluoroethylene. All these compounds were of a high purity grade, and the absence of any impurities was ascertained by vapor phase chromatography.

The experimental results are given in Table III. The reproducibility was most satisfactory, and in all cases, except those of 1-butene, isopropyl ethylene, the 2-butenes and 2,3-pentadiene, no trend in k_2/k_1 's values was observed on increasing the concentration of the substrate. The trend observed for the latter compounds apparently is due to hydrogen abstraction from the substrate, and for the sake of illustration the data obtained for 1-butene are collected in Table IV. The plots of the reciprocals of the apparent k_2/k_1 values versus X_A/X_S gave straight lines and from their intercepts and slopes the relevant k_2/k_1 , k_3/k_2 and k_3/k_1 ratios have been determined. Thus, extrapolated k_2/k_1 's are given in Table III and the k_3/k_2 's and k_3/k_1 's in Table V.

TABLE IV

The Effect of H Abstraction from the Substrate Substrate, butene-1, $T = 65^{\circ}$

		,	
Butene-1.	(CF ₃ H/N ₂)f	$(CF_3H/N_2)_f$	K _A
mole %	(relative)	$(CF_{3}H/N_{2})_{b} - (CF_{3}H/N_{2})_{t}$	$\zeta_{\rm S}$
0.000	0.252^{a}		
.000	.253*	· · · · · · · · ·	
.000	$.251^{a}$		
.062	.180	$1.59 imes 10^{-3}$	
.127	.144	$1.69 imes 10^{-3}$	
.128	.146	$1.75 imes 10^{-3}$	
.174	.127	1.77×10^{-3}	
.218	.118	1.93×10^{-3}	
.276	.121	$2.55 imes10^{-3}$	
^a These	are (CF ₃ H/N	2)6.	

TABLE V

Relative Rates of Abstraction of H from the Substrates (k_3)

Substrate	Type of H	k3/k2	k3/k1	k3/k1 per react. H
cis-Butene-2	Primary	0.315	183	30.4
trans-Butene-2	Primary	.332	194	32.3
CH3·CH=C=CCH3	Primary	.121	50	8.3
Butene-1	Secondary	.213	146.5	73.2
iso-C3H5CH=CH2	Tertiary	.098	69.2	69.2

Discussion

Inspection of Table III reveals a few important facts.

1. For all the investigated hydrocarbons the k_2/k_1 's for CF₃ radical addition are considerably larger than the respective k/k_1 's determined for CH_3 radical addition. This point is emphasized in Table VI where the following notation has been adopted: k_2/k_1 for the CF₃ addition is denoted as $k_{add,CF_s}/k_{abs,CF_s}$, while the respective ratio for the CH₃ radical addition is denoted as $k_{add,CH_2}/k_{abs,CH_2}$. It is probable that the absolute rate constant k_{abs,CF_s} is larger than k_{abs,CH_s} , which would mean that the increase in the k_{add,CF_2} , as compared with the corresponding $k_{\text{add,CH}_3}$, is even larger than appears from the data listed in Table VI. Actually, Steacie and his school⁸ as well as Pritchard and Trotman-Dickenson⁹ determined for various hydrocarbons the ratios of the rate constants of H abstraction by CF₃ to the square root of their rate constant of recombination $(k_{abs}/k_{recom})^{1/2}$. Since the work of Ayscough¹⁰ showed that CF₃ radicals recombine as fast as CH₃ radicals and require no activation energy for recombination, the absolute values of $k_{abs,CF}$, could be calculated. These data are given by Trotman-Dickenson¹¹ who compares

(8) (a) P. B. Ayscough, J. Polanyi and E. W. R. Steacie, Can. J. Chem., 33, 743 (1955); (b) P. B. Ayscough and E. W. R. Steacie, *ibid.*, 34, 103 (1956).

(9) H. O. Pritchard, G. O. Pritchard, H. I. Schiff and A. D. Trotman-Dickenson, Trans. Faraday Soc., 52, 849 (1956).

(10) P. B. Ayscough, J. Chem. Phys., 24, 944 (1956).

them with $k_{abs,CF_{s}}$ and shows the inequality $k_{abs,CH_{s}} < k_{abs,CF_{s}}$. However, recent studies by Pritchard and Dacey¹² as well as the results of this work cast some doubts on Ayscough's results. It seems that the recombination of CF₃ radicals does require activation energy and hence the absolute values $k_{abs,CF_{s}}$ given by Trotman-Dickenson may be too high. Nevertheless, we believe that the inequality $k_{abs,CF_{s}} > k_{abs,CH_{s}}$ does hold.

2. For the series ethylene, propylene and isobutene the increase in the respective $k_{add,CF}$, is much greater than in the corresponding $k_{add,CH}$. (see columns 3 and 5 of Table VI). It was shown² that the increase observed in the series of the $k_{add,CH}$ may be accounted for quantitatively in terms of hyperconjugation. It is tempting to conclude that the much larger increase in the series of the $k_{add,CF}$ arises from the electron-donating effect of a methyl group and that the strongly electrophilic CF₃ radical readily responds to such an effect. The very slightly nucleophilic CH₃ does not respond at all or at most, the effect slightly reduces the reactivity, opposing the enhancing effect of hyperconjugation.

On comparing the rates of reactions of CH_3 and CF_3 radicals to these 3 substrates one observes an interesting phenomenon; namely, CF_3 radicals seem to be more reactive and also more selective than CH_3 radicals. Usually, an increase in reactivity is associated with a decrease in selectivity. The abnormal situation of CF_3 radicals results, as we have pointed out, from their electrophilicity.

3. The inductive effect of a CH₃ group is illustrated by the difference in the reactivities of ethylene and the 2-butenes. It was shown² that for a great variety of substrates the shielding due to a CH₃ group reduces the rate of addition of methyl radicals to a methylated center by a factor of 6-11. This effect is much less pronounced in CF₃ addition. The inductive effect of a CH₃ group placed on a reaction center seems to counteract the steric effect, making the 2-butenes relatively more reactive towards CF₃ radicals than would be expected from their methyl affinities. The value 0.46 given in the third column of Table VI is obtained directly by comparing the reactivities of the 2-butenes and propylene. This value should be corrected since the addition also involves the 2-carbon atom of propylene. Assuming the reactivity of this center to be about 1/2 that of the 2-butene center (only one methyl group activates the 2-carbon center in propylene whereas 2 methyl groups simultaneously affect the centers in the 2-butenes), a tentative value of 0.6 is derived for the effect observed in the 2-butenes.

4. The effect of polarity is most strikingly illustrated by the reactivity of tetrafluoroethylene. For CH_3 addition C_2F_4 is about 10 times more reactive than ethylene. On the other hand, its reactivity with respect to CF_3 addition is substantially *lower* than that of ethylene. Undoubtedly, the powerful electron-withdrawing action of fluorine atoms strongly influences the addition of the

⁽¹¹⁾ A. D. Trotman-Dickenson, "Free Radicals, An Introduction," Methuen's Publ., 1959, p. 65.

⁽¹²⁾ G. O. Pritchard and J. R. Dacey, Can. J. Chem., 38, 182 (1960).

TABLE VI

Addition of CF	and CH ₈ RADICALS						
Solvent, iso-octane; $T = 65^{\circ}$							
kadd, CF3/kabe, CF3	Relative increase in k _{sdd} ,CF1	kadd, CH3/kabe, CH3	Relative increase in kadd,CH3				
2×225	1.0	2×17.0	1.0				
630	2.8	22.0	1.3				
1720	7.6	36.0	2.1				
687	3.05	26.9	1.6				
704	3.12		• •				
658	2.9	••	.,				
2×290	$0.46^{b} (0.60 ext{ cor.})$	2×1.7	0.08				
2×292	0.46^{b} (0.60 cor.)	2 imes 3.45	0.15^{b}				
290		17.6	••				
412		19.2	• •				
2 imes 62	0.28	2 imes15	0.88				
2 imes 34.3	0.15	2×171	10.0				
	Addition of CF Solvent, iso- $k_{add,CF1}/k_{abe,CF1}$ 2 × 225 630 1720 687 704 658 2 × 290 2 × 292 290 412 2 × 62 2 × 34.3	Addition of CF3 and CH3 Radicals Solvent, iso-octane; $T = 65^{\circ}$ Relative increase $k_{\text{add}, CF1}/k_{\text{abs}}, CF1$ 2×225 1.0 630 2.8 1720 7.6 687 3.05 704 3.12 658 2.9 2×290 0.46^{b} (0.60 cor.) 2×292 0.46^{b} (0.60 cor.) 2×292 0.46^{b} (0.60 cor.) 2×292 0.46^{b} (0.28 cor.) 2×62 0.28 2×34.3 0.15	ADDITION OF CF3 AND CH3 RADICALS Solvent, iso-octane; $T = 65^{\circ}$ Relative increase $k_{\text{add}, CF1}/k_{\text{abs}}, CF1$ Relative increase 2×225 1.0 2×17.0 630 2.8 22.0 1720 7.6 36.0 687 3.05 26.9 704 3.12 658 2.9 2×290 $0.46^{b}(0.60 \text{ cor.})$ 2×1.7 2×292 $0.46^{b}(0.60 \text{ cor.})$ 2×3.45 290 17.6 412 19.2 2×62 0.28 2×15 2×34.3 0.15 2×171				

^a The factor of 2 arises from the existence of 2 centers of the reaction in those symmetrical substrates. The case of allene is undecided. It is not yet clear whether the reaction takes place on the terminal or on the central C-atom. ^b These numbers refer to propylene used as a standard.

electrophilic CF₃ making C_2F_4 less reactive than C_2H_4 in spite of the fact that intrinsically its reactivity is greater. The reactivities of other halogenated olefins are under investigation and the results will be reported later. A similar phenomenon is observed in reactions of acetylene.



5. The electrophilic nature of the CF₃ radical makes the polar structure Olefin⁺, CF₃⁻, important in describing the transition state of the addition reaction. One may expect therefore that the reactivity of an olefin toward CF₃ radical should increase with decreasing ionization potential of the substrate. Figure 1 illustrates this point for a series ethylene, propylene, butene-1 and isobutene, and shows that a linear relation exists

between ionization potential and the log of $k_{CF_1 \text{ addition}}$ per CH₂ center.

6. Finally, the reactivities of allene and 2,3pentadiene deserve some comment. It was claimed by Haszeldine¹³ that CF₃ radicals add to the terminal bonds of allene. If this is the case, one would expect 2,3-pentadiene to be perhaps slightly more reactive than allene. (The increase in the reactivity may be comparable to that observed in the pair 2-butene-ethylene.) On the other hand, the reactivity of 2,3-pentadiene with regard to CH₃ addition should be less than allene by a factor of 8 ± 3 . This certainly is not the case, and it was concluded,^{1d} therefore, that methyl radicals add to the central carbon of allene. The difference in the point of attack again reflects the difference in the polarity of CH₃ and CF₃ radicals.

Hydrogen Abstraction Reaction.—Our investigation of the reactivities of the 2-butenes, 2,3pentadiene and 1-butene provide a few data on the relative rates of metathetic reactions

$$RH + CF_3 \longrightarrow R + HCF_3$$

These data are collected in Table V. They show that abstraction of a hydrogen atom from a C-H bond α to the C=C bond proceeds much faster than abstraction of a tertiary aliphatic hydrogen. The increase in reactivity seems to be larger than that observed in analogous reactions involving CH₃ radicals. It is hoped that the continuation of this work will provide more data on this subject and further discussion at this stage may be premature.

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(13) R. N. Haszeldine, K. Leadham and B. R. Steel, J. Chem. Soc. 2040 (1954).