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Kinetics of Addition of CF_3 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 CF_3H , C_2F_6 and N_2 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%/hour. The ratios $\text{CF}_3\text{H}/\text{N}_2$ and $2\text{C}_2\text{F}_6/\text{N}_2$ are constant and independent of concentration in the range 1.6×10^{-3} – $40 \times 10^{-3} M$, and their sum $(\text{CF}_3\text{H} + 2\text{C}_2\text{F}_6)/\text{N}_2 = 2 \pm 0.03$. Addition of olefins and related substrates greatly reduces the $\text{CF}_3\text{H}/\text{N}_2$ ratio, but the $2\text{C}_2\text{F}_6/\text{N}_2$ is unaffected. Hence, the effect of the concentration and of the added substrates indicates that all the C_2F_6 results from a "cage" recombination. The decrease in the $\text{CF}_3\text{H}/\text{N}_2$ ratio, arising from the addition of suitable substrates, is attributed to the addition reaction $\text{CF}_3 + \text{substrate} \rightarrow \text{substrate}\cdot\text{CF}_3$, (k_2) which competes with the abstraction reaction $\text{CF}_3 + \text{iso-octane} \rightarrow \text{CF}_3\text{H} + \text{iso-octyl radical}$, (k_1) for CF_3 radicals. From the decrease in the $\text{CF}_3\text{H}/\text{N}_2$ 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 : C_2H_4 — 2×225 ; $\text{CH}_2=\text{CH}:\text{CH}_2$ —630; $(\text{CH}_3)_2\text{C}:\text{CH}_2$ —1720; $\text{C}_2\text{H}_5\cdot\text{CH}:\text{CH}_2$ —687; *iso*- $\text{C}_3\text{H}_7\cdot\text{CH}:\text{CH}_2$ —704; *t*- $\text{C}_4\text{H}_9\cdot\text{CH}:\text{CH}_2$ —658; *cis*- $\text{CH}_3\cdot\text{CH}:\text{CH}:\text{CH}_3$ — 2×290 ; *trans*- $\text{CH}_3\cdot\text{CH}:\text{CH}:\text{CH}_3$ — 2×292 ; $\text{CH}_2=\text{C}:\text{CH}_2$ —290; $\text{CH}_2=\text{CH}:\text{C}:\text{CH}:\text{CH}_3$ —412; $\text{CH}\equiv\text{CH}$ — 2×62.5 and $\text{CF}_2=\text{CF}_2$ — 2×34.3 . These values are all greater than the respective methyl affinities. The k_2/k_1 's for CF_3 increase more rapidly in the series ethylene, propylene and isobutene than the respective methyl affinities, but C_2F_4 is *less* reactive than C_2H_4 with regard to CF_3 addition, whereas for CH_2 addition it is 10 times more reactive. These results show the strongly electrophilic character of CF_3 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 OCH_3 or $\text{N}(\text{CH}_3)_2$. 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 CF_3 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 CF_3 radicals to some olefins and their halogen derivatives. These data show clearly the strong electrophilic character of CF_3 radicals. It is hoped that the continuation of this work will provide much data of value in

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 IF_5 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 fractionated. 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, CF_3H , C_2F_6 and N_2 . These, as well as the undecomposed hexafluoroazomethane, were transferred by a toepfer 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-

(1) (a) M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 1949 (1955); (b) R. P. Buckley and M. Szwarc, *Proc. Roy. Soc. (London)*, **A240**, 396 (1957); (c) M. Gazith and M. Szwarc, *J. Am. Chem. Soc.*, **79**, 3339 (1957); (d) A. Rajbenbach and M. Szwarc, *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).

(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, C₂F₆ 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-spectrographic 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 gas-chromatographic 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 C₂F₆ and N₂ 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 CF₃H/N₂ and C₂F₆/N₂ were required. As the relative ratios are sufficient for calculating the relative rate constants of addition of CF₃ 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 × 10⁻³, 8 × 10⁻³ and 40 × 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°

[CF ₃ N ₂ CF ₃] M × 10 ³	Time of photolysis, hr.	CF ₃ H N ₂	2C ₂ F ₆ N ₂	CF ₃ 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 CF₃H or as C₂F₆. This means that under our experimental conditions all the radicals which escaped the "cage" recombination reacted with the solvent according to



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 C₂F₆/N₂ 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 ~25% of CF₃ 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 II

THE EFFECT OF ADDED ISO-BUTENE ON THE PHOTOLYSIS OF
CF₃·N₂·CF₃

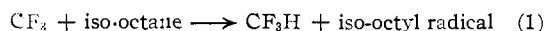
Solvent, iso-octane; T = 65°

Mole % of iso-butene	CF ₃ H/N ₂	2(C ₂ F ₆)/N ₂	k ₂ /k ₁
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 ^a	.475 ^a	1784
.097	.608 ^a	.492 ^a	1655
.131	.503 ^a	.480 ^a	1573
.165	.416 ^a	.472 ^a	1700
.210	.351 ^a	.490 ^a	1693

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

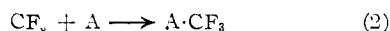
Our results differ from those obtained by Dacey and Young.⁶ Those workers photolyzed gaseous hexafluoro-azomethane in the absence of any diluent. They found that under their conditions CF₃ radicals may dimerize or add to the undecomposed azo-compound, the latter reaction producing (CF₃)₂N·N(CF₃)₂ or [(CF₃)₂N·N(CF₃)₂]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 (10³-10⁴) 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 CF₃ Radical Addition.—It was shown in the preceding section that all the CF₃ radicals generated in the photolysis either abstract hydrogen atoms from the solvent and form CF₃H



or undergo a "cage" recombination which converts a constant fraction of the CF₃ radicals into C₂F₆. 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 CF₃H/N₂ ratio resulting from the presence of a suitable substrate A is due to the reaction



In view of the low stationary concentration of all the radicals present in the system, the recombination of CF₃ radicals with A·CF₃ 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 CF₃, making the A·CF₃ 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 (CF₃H/N₂)_t the fraction of CF₃ radicals reacting with the solvent according to equation 1 and by CF₃·A/N₂ that fraction reacting with A according to equation 2, then

$$(\text{CF}_3\cdot\text{A}/\text{N}_2)/(\text{CF}_3\text{H}/\text{N}_2)_t = (k_2/k_1)(X_A/X_S)$$

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, (CF₃·A/N₂) may be found from the equation

$$(\text{CF}_3\cdot\text{A}/\text{N}_2) = (\text{CF}_3\text{H}/\text{N}_2)_b - (\text{CF}_3\text{H}/\text{N}_2)_t$$

where (CF₃H/N₂)_b represents the respective product ratio in a "blank," *i.e.* in an experiment performed in the absence of A. It follows, therefore, that

$$k_2/k_1 = \{[(\text{CF}_3\text{H}/\text{N}_2)_b - (\text{CF}_3\text{H}/\text{N}_2)_t]/(\text{CF}_3\text{H}/\text{N}_2)_t\}(X_S/X_A)$$

Variation of the mole ratio X_S/X_A left k₂/k₁ 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 k₂/k₁ (for butene-2) is independent of [CF₃N₂CF₃]. The latter was changed from 2.8 × 10⁻⁵ M to 12.4 × 10⁻⁵ M.

Our treatment involves the assumption that only the addition of CF₃ 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



Such a situation was considered in reference 1c,

TABLE III

RELATIVE RATES OF ADDITION OF CF₃ RADICALS (k₂) AT 65° GIVEN IN THE FORM OF k₂/k₁ WHERE k₁ REFERS TO THE REACTION CF₃ + C₈H₁₈ → CF₃H + C₈H₁₇

Substrate	Range of conc. in mole fraction × 10 ³	No. of expts.	k ₂ /k ₁
C ₂ H ₄ (I series)	1.5-7.0	5	452 ± 12
C ₂ H ₄ (II series)	0.6-2.0	4	447 ± 31
C ₂ H ₄ (III series)	1.0-4.0	5	468 ± 35
CH ₃ CH=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) ₂ C=CH ₂ (I series)	0.5-2.0	5	1681 ± 75
(CH ₃) ₂ C=CH ₂ (II series)	.5-2.0	5	1642 ± 44
(CH ₃) ₂ C=CH ₂ (III series)	.5-10.0	5	1721 ± 23 ^a
C ₂ H ₅ ·CH=CH ₂	.6-2.6	6	687 extrp. to 0%
<i>iso</i> -C ₃ H ₇ ·CH=CH ₂	.7-2.8	5	704 extrp. to 0%
<i>t</i> -C ₄ H ₉ ·CH=CH ₂	2.0-10.0	6	658 ± 11
<i>cis</i> -CH ₃ ·CH=CH·CH ₃	0.5-3.0	12	580 extrp. to 0%
<i>trans</i> -CH ₃ ·CH=CH·CH ₃	0.6-3.0	6	585 extrp. to 0%
CH ₂ =C=CH ₂ (I 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 ₃ F ₄	3.2-11.5	6	68.6 ± 4.2

^a 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

$$\{(\text{CF}_3\text{H}/\text{N}_2)_t/[(\text{CF}_3\text{H}/\text{N}_2)_b - (\text{CF}_3\text{H}/\text{N}_2)_t]\}(X_A/X_S)$$

varies linearly with X_A/X_S, the intercept of the resulting straight line giving k₁/k₂ while its slope represents k₃/k₂. Such situations were encountered when substrates such as butene-1 or butene-2 were investigated.

Finally, it should be emphasized that the calculation of k₂/k₁ or k₃/k₂ 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 k₂/k₁'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, mole %	$(CF_3H/N_2)_t$ (relative)	$\frac{(CF_3H/N_2)_t}{(CF_3H/N_2)_b - (CF_3H/N_2)_t} \cdot \frac{X_A}{X_S}$
0.000	0.252 ^a
.000	.253 ^a
.000	.251 ^a
.062	.180	1.59×10^{-3}
.127	.144	1.69×10^{-3}
.128	.146	1.75×10^{-3}
.174	.127	1.77×10^{-3}
.218	.118	1.93×10^{-3}
.276	.121	2.55×10^{-3}

^a These are $(CF_3H/N_2)_b$.

TABLE V

RELATIVE RATES OF ABSTRACTION OF H FROM THE SUBSTRATES (k_3)

Substrate	Type of H	k_3/k_2	k_3/k_1	k_3/k_1 per react. H
<i>cis</i> -Butene-2	Primary	0.315	183	30.4
<i>trans</i> -Butene-2	Primary	.332	194	32.3
CH ₃ ·CH=C=CCH ₃	Primary	.121	50	8.3
Butene-1	Secondary	.213	146.5	73.2
<i>iso</i> -C ₃ H ₅ CH=CH ₂	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 CH₃ 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 $k_{add,CF_3}/k_{abs,CF_3}$, while the respective ratio for the CH₃ radical addition is denoted as $k_{add,CH_3}/k_{abs,CH_3}$. It is probable that the absolute rate constant k_{abs,CF_3} is larger than k_{abs,CH_3} , which would mean that the increase in the k_{add,CF_3} , as compared with the corresponding k_{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_3} 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,CH_3} and shows the inequality $k_{abs,CH_3} < k_{abs,CF_3}$. 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_3} given by Trotman-Dickenson may be too high. Nevertheless, we believe that the inequality $k_{abs,CF_3} > k_{abs,CH_3}$ does hold.

2. For the series ethylene, propylene and isobutene the increase in the respective k_{add,CF_3} is much greater than in the corresponding k_{add,CH_3} (see columns 3 and 5 of Table VI). It was shown² that the increase observed in the series of the k_{add,CH_3} 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_3} 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 CH₃ and CF₃ radicals to these 3 substrates one observes an interesting phenomenon; namely, CF₃ radicals seem to be more reactive and also more selective than CH₃ radicals. Usually, an increase in reactivity is associated with a decrease in selectivity. The abnormal situation of CF₃ 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 CH₃ addition C₂F₄ is about 10 times more reactive than ethylene. On the other hand, its reactivity with respect to CF₃ 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_3 AND CH_3 RADICALS
Solvent, iso-octane; $T = 65^\circ$

Substrate	$k_{\text{add},\text{CF}_3}/k_{\text{abs},\text{CF}_3}$	Relative increase in $k_{\text{add},\text{CF}_3}$	$k_{\text{add},\text{CH}_3}/k_{\text{abs},\text{CH}_3}$	Relative increase in $k_{\text{add},\text{CH}_3}$
$\text{CH}_2:\text{CH}_2^a$	2×225	1.0	2×17.0	1.0
$\text{CH}_3\cdot\text{CH}:\text{CH}_2$	630	2.8	22.0	1.3
$(\text{CH}_3)_2\text{C}:\text{CH}_2$	1720	7.6	36.0	2.1
$\text{C}_2\text{H}_5\cdot\text{CH}=\text{CH}_2$	687	3.05	26.9	1.6
<i>iso</i> - $\text{C}_3\text{H}_7\cdot\text{CH}=\text{CH}_2$	704	3.12
<i>t</i> - $\text{C}_4\text{H}_9\cdot\text{CH}=\text{CH}_2$	658	2.9
<i>cis</i> - $\text{CH}_3\cdot\text{CH}=\text{CH}\cdot\text{CH}_3^a$	2×290	0.46^b (0.60 cor.)	2×1.7	0.08^b
<i>trans</i> - $\text{CH}_3\cdot\text{CH}=\text{CH}\cdot\text{CH}_3^a$	2×292	0.46^b (0.60 cor.)	2×3.45	0.15^b
$\text{CH}_2:\text{C}:\text{CH}_2$	290	..	17.6	..
$\text{CH}_3\cdot\text{CH}:\text{C}:\text{CH}\cdot\text{CH}_3$	412	..	19.2	..
$\text{CH}\equiv\text{CH}^a$	2×62	0.28	2×15	0.88
$\text{CF}_2:\text{CF}_2^a$	2×34.3	0.15	2×171	10.0

^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 CF_3 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.

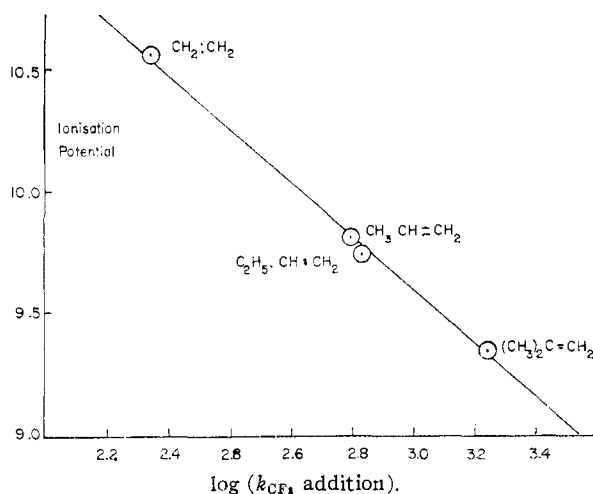


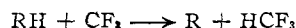
Fig. 1.

5. The electrophilic nature of the CF_3 radical makes the polar structure Olefin^+ , CF_3^- , important in describing the transition state of the addition reaction. One may expect therefore that the reactivity of an olefin toward CF_3 radical should increase with decreasing ionization potential of the substrate. Figure 1 illustrates this point for a series ethylene, propylene, butene-1 and iso-butene, and shows that a linear relation exists

between ionization potential and the log of k_{CF_3} addition per CH_2 center.

6. Finally, the reactivities of allene and 2,3-pentadiene deserve some comment. It was claimed by Haszeldine¹³ that CF_3 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 CH_3 addition should be less than allene by a factor of 8 ± 3 . This certainly is not the case, and it was concluded,¹⁴ 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 CH_3 and CF_3 radicals.

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



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 CH_3 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.

In conclusion the financial support of this work by the National Science Foundation is gratefully acknowledged.

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