Activation Energies and Entropies of Activation of CF_3 Radical Addition

Part 1.—Gas Phase

BY J. M. PEARSON AND M. SZWARC

Dept. of Chemistry, State University College of Forestry at Syracuse University, Syracuse 10, New York

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The enthalpies and entropies of activation of CF_3 radical addition to a series of substrates possessing the $CH_2{=}C\langle$ reaction centre were determined in the gas phase between 65 and 180°C. The addition process, $\rangle C{=}CH_2+CF_3\rightarrow\rangle\dot{C}{-}CH_2CF_3$, (2), competes for CF_3 radicals with the hydrogen abstraction, $RH+CF_3\rightarrow R\cdot+CF_3H$, (1), RH denoting 2,3-dimethyl butane. The radicals were formed by photolysis of $CF_3NN.CF_3$. The system was found free of any side reactions. The following substrates were investigated: vinyl fluoride, vinyl chloride, ethylene, propylene, isobutene, styrene, α-methyl styrene, 1,3-butadiene, isoprene and 2,3-dimethyl-1,3-butadiene.

The reactivities, measured by k_2/k_1 at 65°C, increase 200-fold when the least reactive vinyl fluoride is compared with the most reactive 2,3-dimethyl butadiene-1,3. This increase is due to a decrease in the activation energies, $-\Delta E = (E_2-E_1)$ whereas the A_2/A_1 factors remained essentially constant. Good agreement was found between these A_2/A_1 values and those found in the addition of CH_3 radicals to the same series of substrates.

The CF_3 radical additions to a series of olefinic, acetylenic and aromatic substrates were studied [1-4] to establish the reactivity pattern as a function of substrates structure. The relative rate constants k_2 of CF_3 addition at 65°C,

$$CF_3+\text{substrate}\rightarrow CF_3\,.\,\text{substrate}\cdot \qquad k_2,$$

were chosen to measure the substrate reactivities. Reaction (2) competed for CF_3 with the hydrogen abstraction (1),

$$CF_3+HS\rightarrow CF_3H+S\cdot, \qquad k_1,$$

HS being an aliphatic hydrocarbon used as a solvent in the liquid phase or as a diluent in the gas phase. The result gave k_2/k_1; however, since the same aliphatic hydrocarbon, HS, was used in each series of experiments, the variation of k_2/k_1 reflected the changes of k_2.

The experimental technique, described previously,[1] was applied for solution studies of the following substrates: mono-olefinic hydrocarbons,[1] non-substituted aromatic hydrocarbons,[2] mono- and di-substituted benzenes,[3] and fluorinated and chlorinated olefins.[5] With some modification this technique was adopted to study the gas phase addition,[4] and thus the ratios $(k_2/k_1)_l/(k_2/k_1)_g$ were determined at 65°C. The results showed [4] that k_2/k_1 were always slightly larger in the liquid than in the gas phase; for nonpolar substrates $(k_2/k_1)_l/(k_2/k_1)_g$ was 1·1-1·2.

In the present investigations it was intended (i) to determine the activation energies, E_2-E_1, and the temperature independent factors, A_2/A_1, for CF_3 addition to a series of substrates possessing the same reactive centre; and (ii) to compare the activation energies and *A* factors for reactions proceeding in the gas phase and in solution. The results for the gas phase are reported in this paper, and those for the solution in the following one.

EXPERIMENTAL

All compounds were better than 99 % pure, and 2,3-dimethyl butane, free of any trace of olefin, was used as a diluent. The reaction proceeded in cylindrical Pyrex bulbs of about 750 cm^3 volume each equipped with a breakseal to facilitate the withdrawal of the products. The constant temperature bath was filled with silicon oil and could be heated to 180°C. The temperature was kept constant with ±1°C. A high-pressure G.E. AH-6 mercury lamp, placed in a well in the centre of the bath, was used as the light source.

CF_3 radicals were generated by photolysis of hexafluoroazomethane, each irradiation lasting for about 8–12 h. The analysis of the products was performed on a high-vacuum line; the composition of a mixture of CF_3H and N_2 was determined by gas chromatography. No C_2F_6 was detected in any experiment. The description of the ampoule-filling procedure and of the analytic technique is given in ref. (4).

RELIABILITY OF THE SYSTEM

Side reactions often accompany the main process; the effect on the numerical value of a rate constant may be small, but the apparent activation energy might be considerably changed. It is, therefore, important to check the reliability of the chosen system at the lowest and highest temperatures used and to establish the validity of all the assumptions introduced in the treatment of the experimental data.

Our method of calculation is based on the assumption that *all* the CF_3 radicals produced by photolysis react either with the aliphatic hydrocarbon and yield CF_3H through reaction (1), or add to the substrate in reaction (2). *None* of the CF_3 radicals should react with hexafluoroazomethane, with any product of the photolysis or with any radical present in the system.

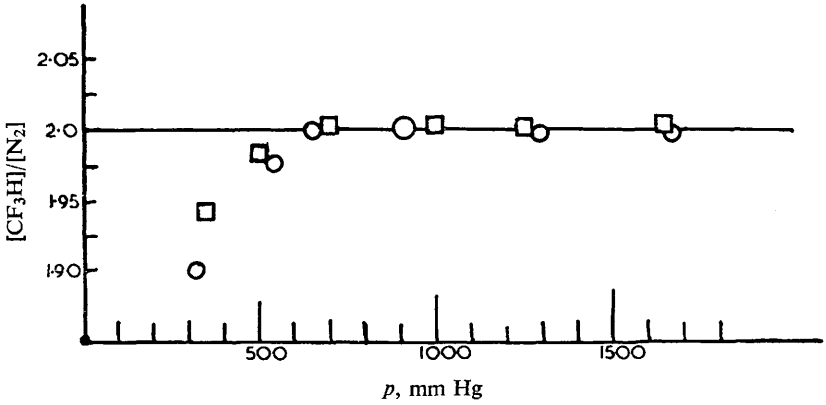

FIG. 1.—Effect of total pressure on $[CF_3H]/[N_2]$.
○ at 180°C, □ at 65°C.

Under our standard conditions of irradiation and for $p_{CF_3N_2CF_3} \approx 0{\cdot}5$ mm Hg and $p_{DMB} \approx 700$ mm Hg, the CF_3 radicals neither add to the azo-compound nor combine with other radicals. This is proved by experiments, carried out in the absence of any substrate, in which the partial pressure p_{DMB}, of 2,3-dimethyl butane, was varied from 300 to 1500 mm Hg. No trace of C_2F_6 was found * and, as shown by fig. 1, the ratio $CF_3H/N_2 = 2$, if $p_{DMB} > 500$ mm Hg. Hence, at 65°C as well as at 180°C, *all* the CF_3 radicals formed by the photolysis react with the butane if its partial pressure exceeds 500 mm Hg. Addition of a substrate increases the rate of CF_3 consumption and makes the losses less probable. At $p_{DMB} \approx 350$ mm Hg the loss of CF_3 was only ~ 3 % at 65°C although it exceeded 5 % at 180°C. The reaction causing the loss requires a greater activation energy than reaction (1), and tentatively it is identified as [6, 7]

$$CF_3 + CF_3 . N_2CF_3 \rightarrow (CF_3)_2 . N_2 . CF_3$$

Hexafluoroazomethane (partial pressure 0·2-0·6 mm Hg) was photolyzed at 65 and 180°C in pure vinyl fluoride, the least reactive substrate, and in isobutene. Although the partial pressure of the substrate was only 200 mm Hg neither CF_3H nor C_2F_6 was found in the products.

This proves that either reaction (2) is much faster than the disproportionation,

$$CF_3 + CF_3 . \text{substrate} \rightarrow CF_3H + CF_3\text{—substituted olefin},$$

or the disproportionation is negligible in respect to combination. The constancy of k_2/k_1 for variable ratio [substrate]/[HS] (see table 3), proves that the reactions

$$CF_3 + S\cdot \rightarrow CF_3H + \text{olefin}$$

and

$$CF_3 + CF_3A\cdot \rightarrow CF_3 . A . CF_3$$

also are insignificant under our experimental conditions, since the occurrence of either reaction would lead to an increase in k_2/k_1 with increasing ratio [substrate]/[HS]. Hence, *all* the CF_3 . are consumed in reaction (2).

The other assumption, tacitly introduced, implies the irreversibility of the addition, i.e., the adduct radical, CF_3 . substrate, must not decompose into CF_3 + substrate. This was verified in two ways. The adduct radical eventually disappears from the system either through its interaction with other radicals or with the diluent,

$$CF_3 . \text{substrate}\cdot + HS \rightarrow CF_3 . \text{substrate} . H + S\cdot .$$

The probability of its decomposition into CF_3 + substrate increases therefore with its average life time, which may be prolonged by decreasing the partial pressure of hexafluoroazomethane at constant light intensity and constant total pressure, or by decreasing the total pressure keeping all the other parameters constant. The decomposition regenerates a CF_3 which may then react with HS to yield CF_3H or with the substrate to form again the adduct radical. An increase of the $[CF_3H]/[N_2]$ ratio on increasing the life time of the adduct radical at a constant ratio [substrate]/[HS] would be, therefore, the clearest manifestation of its dissociation.

Experiments were therefore performed keeping constant the partial pressures of 2,3-dimethylbutane and of the substrate but varying the partial pressure of hexafluoroazomethane by approximately a factor of ten. The results in table 1 show that the ratio $[CF_3H]/[N_2]$ remained constant and independent of the partial pressure of hexafluoroazomethane even at 180°C when the dissociation should be favoured. Various substrates were used, viz., propylene, styrene, vinyl fluoride and benzene, and a constant CF_3H/N_2 ratio is found even when the substrate forms a relatively weak CF_3—substrate bond, e.g., for vinyl fluoride at 180°C or benzene at 65°C. At 150°C there is evidence of a slight decomposition of the benzene . CF_3 adduct, as expected from the very low dissociation energy of the C_6H_6—CF_3 bond.[8]

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* Our analytic technique allows us to determine the ratio C_2F_6/N_2 as low as 0·005.

The effect of the partial pressure of dimethylbutane was investigated by keeping the ratio [substrate]/[HS] constant but varying the total pressure. The ratio $[CF_3H]/[N_2]$ remained constant (see table 2) and independent of the total pressure for the constant ratio substrate/HS, or alternatively the calculated k_2/k_1 remained constant when the total pressure and the ratio [substrate]/[HS] were varied.

TABLE 1.—STUDIES ON THE REVERSIBILITY OF CF_3 RADICAL ADDITION
EFFECT OF VARIATIONS OF THE PARTIAL PRESSURE OF $CF_3N_2CF_3$ ON
THE RATIO $[CF_3H]/[N_2]$

Diluent, 2,3-dimethyl butane; volume of reaction vessel ~750 cm³; P_{total}~ 1000 mm Hg

$T = 180°C$

PROPYLENE; [HS]/[A] = 33·44

HFAM moles × 10^5	0·77	1·92	3·08	5·39	6·93
$[CF_3H]/[N_2]$	1·01 ‡	1·07	1·04	1·08	1·06

STYRENE; [HS]/[A] = 131·3

HFAM moles × 10^5	0·77	1·92	3·08	5·39	6·93
$[CF_3H]/[N_2]$	1·04 ‡	1·12	1·11	1·14	1·13

VINYL FLUORIDE; [HS]/[A] = 5·71

HFAM moles × 10^5	1·92	1·92	3·08	3·08	7·68
$[CF_3H]/[N_2]$	1·06	1·08	1·04	1·06	1·07

$T = 65°C$

BENZENE; [HS]/[A] = 1·06 *

HFAM moles × 10^5	0·248	1·54	2·56
$[CF_3H]/[N_2]$	0·835	0·823	0·854

$T = 150°C$

BENZENE; [HS]/[A] = 1·05

HFAM moles × 10^5	1·07	1·83	6·40	10·1
$[CF_3H]/[N_2]$	1·15	1·10	1·05	1·01

* P_{total}~400 mm Hg.

‡ The small amount of products produced in these experiments may lead to some loss of CF_3H and consequently to a ratio $[CF_3H]/[N_2]$ slightly lower than anticipated.

TABLE 2.—STUDIES ON THE REVERSIBILITY OF CF_3 RADICAL ADDITION
EFFECT OF VARIATIONS IN THE TOTAL PRESSURE OF THE SYSTEM ON
RATIO $[CF_3H]/[N_2]$

Substrate, vinyl fluoride; diluent, 2,3-dimethylbutane; volume of reaction vessel~ 750 cm³

$\frac{[HS]}{[substrate]}$	P_{total} mm Hg	°C	HFAM moles × 10^5	$[CF_3H]/[N_2]$	$\frac{k_2}{k_1}$
6·38	~ 500	65	1·92	0·95	7·0
6·38	~ 500	65	7·68	0·96	
6·38	~ 600	180	1·92	1·09	5·2
6·38	~ 600	180	7·68	1·11	
6·38	~ 1000	65	1·92	0·93	7·2
6·38	~ 1000	65	7·68	0·95	
6·38	~ 1700	180	1·92	1·11	5·0
6·38	~ 1700	180	7·62	1·12	
4·57	~ 550	180	1·15	0·96	5·0
4·57	~ 550	180	3·84	0·98	
4·57	~ 550	180	6·14	0·95	

Hence under our experimental conditions CF_3H is formed entirely by reaction (1) and the " loss " of CF_3 arises only from reaction (2). Moreover, for all the substrates for which the activation energies were determined, reaction (2) is irreversible even at 180°C. The reported values of E_2-E_1 are therefore not distorted by any side reactions.

RESULTS

We determined the k_2/k_1 values for substrates possessing a terminal $CH_2{=}C\langle$ group as the reaction centre, viz., vinyl fluoride, vinyl chloride, ethylene, propylene, isobutene, styrene, α-methyl styrene, 1,3-butadiene, isoprene and 2,3-dimethyl-1,3-butadiene. The results are collected in table 4, and their reproducibility and independence on the ratio diluent/substrate is shown by examples given in table 3.

TABLE 3

$P_{\text{total}} \sim 700$ mm Hg

VINYL FLUORIDE, 65°C					
[HS]/[A]	4·39	9·18	13·36	20·27	
k_2/k_1	7·1	7·2	6·4	7·7	average 7·1 ±0·3
VINYL FLUORIDE, 150°C					
[HS]/[A]	3·00	6·24	9·08	13·77	
k_2/k_1	5·0	5·0	5·1	5·3	average 5·1 ±0·1
ISOBUTENE, 65°C					
[HS]/[A]	102	214	311	472	
k_2/k_1	279	284	258	274	average 274 ±6
ISOBUTENE, 180°C					
[HS]/[A]	32·8	68·5	99·7	147	
k_2/k_1	73·1	68·5	69·8	74·4	average 71·5 ±3
2,3-DIMETHYL BUTADIENE, 65°C					
[HS]/[A]	381	508	762	1525	
k_2/k_1	1568	1598	1525	1542	average 1560 ±25
2,3-DIMETHYL BUTADIENE, 180°C					
[HS]/[A]	381	508	762	1525	
k_2/k_1	292	294	284	271	average 285 ±6

Some modifications of the experimental technique were necessary for ethylene. Its high volatility led to dilution of the collected mixture, and, therefore the amounts of CF_3H and N_2 which could be analyzed were decreased. Moreover, ethylene and CF_3H were not sufficiently well resolved on the chromatogram. Hence, the ampoules containing the samples were opened into a trap containing an excess of previously de-aerated Br_2 in order to remove ethylene. Since the diluent, 2,3-dimethyl butane, also rapidly reacts with Br_2 giving HBr, the gas sample was subsequently passed through a KOH trap where HBr was removed. The remaining CF_3H and N_2 were then pumped into a mixing chamber and thereafter analyzed in the usual way. This technique gave reproducible results without any loss of gas.

Arrhenius plots, shown in fig. 2, illustrate the reliability of the results. The activation energies $-(E_2-E_1)$ and the ratio of A factors A_2/A_1 calculated by the least square method, are given in table 5. The $-\Delta E$ values are accurate within

TABLE 4.—ADDITION OF CF_3 RADICALS TO OLEFINS AND DIENES IN THE GAS PHASE

CF_3+2,3-dimethyl butane→CF_3H+radical . . . k_1

CF_3+olefin→CF_3 . olefin· . . . k_2

substrate	mole fraction substrate	no. of expt.	T°C	k_2/k_1
vinyl fluoride	0·05-0·32	4	65	7·1 ±0·50
,,	0·07-0·31	4	100	5·5 ±0·25
,,	0·07-0·33	4	150	5·2 ±0·10
,,	0·15-0·22	3	180	4·9 ±0·10
vinyl chloride	0·012-0·040	4	65	36·7 ±1·0
,,	0·012-0·040	4	120	24·6 ±0·8
,,	0·0095-0·032	4	180	18·6 ±0·5
ethylene	0·012-0·055	4	65	74·8 ±1·5
,,	0·014-0·065	4	120	48·7 ±2·0
,,	0·019-0·090	4	183	29·2 ±1·5
propylene	0·007-0·030	4	65	92·6 ±1·5
,,	0·008-0·037	4	95	60·8 ±1·0
,,	0·015-0·069	4	120	45·9 ±1·0
,,	0·024-0·11	4	180	32·7 ±1·5
isobutene	0·0021-0·010	4	65	274 ±6
,,	0·0052-0·025	4	120	140 ±6
,,	0·0070-0·030	4	180	71·5 ±3
styrene	0·0013-0·0040	3	65	404 ±8
,,	0·0026-0·0052	4	115	217 ±12
,,	0·0052-0·013	4	150	147 ±8
α-methyl styrene	0·0008-0·0032	4	65	648 ±15
,,	0·0008-0·0032	4	120	285 ±7
,,	0·0035-0·014	4	175	160 ±8
butadiene	0·0016-0·0073	4	65	742 ±2
,,	0·003-0·013	4	125	309 ±12
,,	0·004-0·020	4	175	187 ±8
isoprene	0·0009-0·0052	4	65	1090 ±20
,,	0·0009-0·0052	4	95	672 ±10
,,	0·0023-0·0046	4	180	233 ±7
2,3-dimethylbutadiene	0·0006-0·0026	4	65	1560 ±25
,, ,,	0·0006-0·0026	3	95	930 ±20
,, ,,	0·0006-0·0026	4	180	285 ±6

TABLE 5.—ACTIVATION ENERGY AND A FACTORS

CF_3+substrate→CF_3. substrate . . . k_2

CF_3+dimethyl-butane→CF_3H+radical . . . k_1

substrate	k_2/k_1, gas 65°C	$-(E_2-E_1)$ kcal/mole	A_2/A_1
vinyl fluoride	7·1	1·02	1·55
vinyl chloride	36·8	1·84	2·40
ethylene	74·6	2·35	2× 1·17
propylene	92·6	2·76	1·52
isobutylene	274	3·52	1·46
styrene	404	3·45	2·45
α-methylstyrene	648	3·86	2·14
1,3-butadiene	742	3·78	2× 1·40
isoprene	1090	4·05	2× 1·35
2,3-dimethyl-1,3-butadiene	1560	4·42	2× 1·20

±0·10-0·20 kcal/mole. In spite of a 200-fold variation in the reactivity of the substrates the A factors are approximately constant and vary randomly between 1·17 and 2·45, the average value of A_2/A_1 being 1·66.

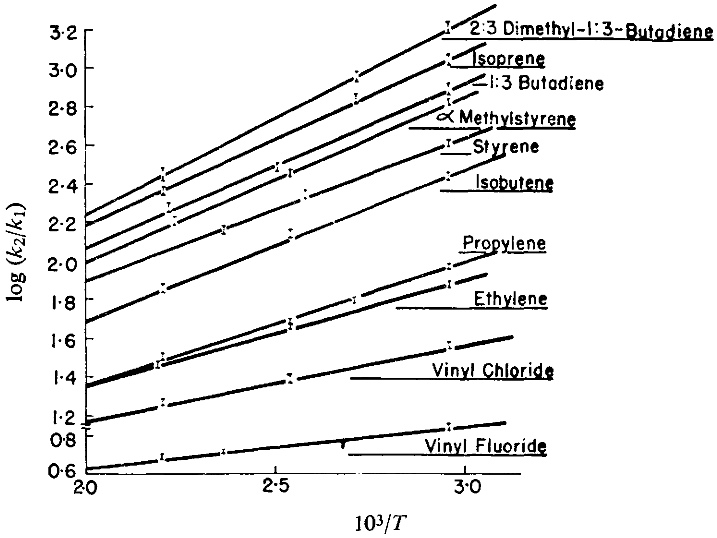


FIG. 2.—An Arrhenius plot of k_2/k_1 for the substrates in the gaseous phase.

DISCUSSION

In a series of similar reactions involving identical reaction centres the variations in the rate constants are caused by changes in the respective activation energies, whereas the A factors remain essentially constant (table 5).

A similar situation was observed in the addition of CH_3 radicals to the same series of substrates.[9] This reaction was studied in iso-octane solution between 0 and 95°C. A hundred-fold variation in the respective rate constants resulted from a change by 2·3 kcal/mole in the activation energies; however, $A_{2,CH_3}/A'_{1,CH_3}$ remained again approximately constant, randomly varying within 30 % of the average value of 6·4.

To compare the reactions of CF_3 radical with those of CH_3 radical, the ratios k_1/k'_1 were determined, the constant k'_1 referring to the reaction

$$CF_3 + \text{iso-octane} \rightarrow CF_3H + \text{iso-octyl radical} \quad k'_1.$$

The photolysis of hexafluoro-azomethane was investigated therefore in iso-octane vapour at 110 and 180°C keeping the pressure of the hydrocarbon above 760 mm Hg. No C_2F_6 was formed and the ratio $[CF_3H]/[N_2]$ was $2·0 \pm 0·1$, showing that this system also is suitable for our studies. The ratio of k_2/k'_1 was then determined for propylene and found to be 230 at 110°C and 115 at 180°C. This leads to $E_2 - E'_1 = -3·2$ kcal/mole compared to the respective $E_2 - E_1 = -2·8$ kcal/mole for 2,3-dimethyl-butane. It follows that $E'_1 - E_1 = 0·4$ kcal/mole and $A_1/A'_1 = 2 \times 1·2$. The statistical factor of 2 arises from the presence of two tertiary C—H in the butane while only one is present in a molecule of iso-octane, $(CH_3)_2 . CH . CH_2 . C(CH_3)_3$.

It seems that the shielding of C—H by the bulky neopentyl group and two methyl groups slightly increases the activation energy of the abstraction and decreases the respective A factor by about 15 %. The average value of A_2/A'_1 is therefore 3·8 for CF_3 radical reacting in the gas phase while the A_2/A'_1 for CH_3 radical reacting in a hydrocarbon solution was found to be 6·4. In a hydrocarbon solution the A_2/A_1 factors are by about 20-30 % higher (part 2) than those observed for the same reactions proceeding in the gas phase, and hence the A_2/A'_1 values for CF_3 and CH_3 radicals are very close (3·8 as compared with 4·8). This result is expected since from transition state theory

$$\{A_{2,\mathrm{CH_3}}/A'_{1,\mathrm{CH_3}}\}/\{A_{2,\mathrm{CF_3}}/A'_{1,\mathrm{CF_3}}\} =$$

$$\frac{f^{\neq}\begin{pmatrix}\mathrm{C}\ldots\mathrm{CH_3}\\ \| \\ \mathrm{C}\end{pmatrix} f(\mathrm{CH_3})f(\mathrm{S{-}H})/f^{\neq}(\mathrm{S{-}H}\ldots\mathrm{CH_3})f(\mathrm{CH_3})f\begin{pmatrix}\mathrm{C}\\ \| \\ \mathrm{C}\end{pmatrix}}{f^{\neq}\begin{pmatrix}\mathrm{C}\ldots\mathrm{CF_3}\\ \| \\ \mathrm{C}\end{pmatrix} f(\mathrm{CF_3})f(\mathrm{S{-}H})/f^{\neq}(\mathrm{S{-}H}\ldots\mathrm{CF_3})f(\mathrm{CF_3})f\begin{pmatrix}\mathrm{C}\\ \| \\ \mathrm{C}\end{pmatrix}} =$$

$$\left[f^{\neq}\begin{pmatrix}\mathrm{C}\ldots\mathrm{CH_3}\\ \| \\ \mathrm{C}\end{pmatrix}/f^{\neq}(\mathrm{S{-}H}\ldots\mathrm{CH_3})\right]/\left[f^{\neq}\begin{pmatrix}\mathrm{C}\ldots\mathrm{CF_3}\\ \| \\ \mathrm{C}\end{pmatrix}/f^{\neq}(\mathrm{S{-}H}\ldots\mathrm{CF_3})\right],$$

where the f denote the respective partition function. The ratio

$$\left[f^{\neq}\begin{pmatrix}\mathrm{C}\ldots\mathrm{CH_3}\\ \| \\ \mathrm{C}\end{pmatrix}/f^{\neq}(\mathrm{S{-}H}\ldots\mathrm{CH_3})\right]/\left[f^{\neq}\begin{pmatrix}\mathrm{C}\ldots\mathrm{CF_3}\\ \| \\ \mathrm{C}\end{pmatrix}/f^{\neq}(\mathrm{S{-}H}\ldots\mathrm{CF_3})\right]$$

should be about unity.

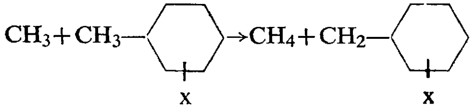
REVIEW OF THE RELATED LITERATURE

It is commonly assumed that in a series of similar reactions the entropy of activation remains constant and Hammett's $\sigma-\rho$ relations are examples justifying this assumption. In radical reactions modification of the molecule in regions outside the reaction centre frequently has a negligible effect on the entropy of activation and often it leaves the rates and activation energies constant.[10] In such a series of reactions, small but systematic errors may sometimes appreciably distort the observed activation energies and then the respective Arrhenius lines cross *within*, or *close to*, the investigated temperature range—a direct mathematical consequence of such errors.

There are, of course, series of reactions in which the variations of activation energies are partially compensated by changes in the entropies of activation, leaving the rates approximately constant. For example, a reaction studied in different solvents may proceed with little change in the rate but with a large variation in the activation energy, due, e.g., to different degrees of solvation of the transition state. However, since solvation also affects the entropy of activation its effect upon $\Delta S^{\neq}$ partially compensates its effect on E. Nevertheless, an exact compensation and just within the investigated temperature range would be unexpected, and whenever the observed rates are closely similar, one may suspect that neither the activation energies nor the entropies of activation had changed to any appreciable degree. Two examples illustrate this point.

Rebbert *et al* [11-13] studied the metathetic reaction, $RH+CH_3 \rightarrow R+CH_4$, for toluene, the xylenes and the fluorotoluenes. They found essentially identical rates for all these processes, correcting for the statistical factor, but claimed variations in the activation energies, up to 2·8 kcal/mole, as shown in table 6. We present their results in the form of an Arrhenius plot in fig. 3; and this plot apparently indicates a nearly constant activation energy for all these processes. It appears that systematic and temperature dependent errors, caused by some side reactions, are responsible for the spread in their E values.

TABLE 6.—DATA OF REBBERT *et al.* FOR THE REACTION

(1)


hydrocarbon	$E_1-\frac{1}{2}E_2$ of Rebbert kcal/mole	$13+\log(k_1/k_2^{\frac{1}{2}})$ at 380°K	at 455°K	$(k_1/k_2^{\frac{1}{2}})\times 10^{13}$ at 380°K	at 455°K
toluene	7·4	0·650	1·353	4·47	22·5
½-p-xylene	7·4	0·699	1·401	5·00	25·2
½-o-xylene	7·8	0·759	1·502	5·74	31·8
½-m-xylene	8·5	0·682	1·490	4·81	30·9
p-F-toluene	5·7	0·749	1·290	5·61	19·5
o-F-toluene	6·0	0·748	1·319	5·60	20·8
m-F-toluene	7·1	0·670	1·344	4·68	22·1
	average	0·708	1·385		

There is no reason for a close compensation of ΔE by $\Delta S^{\neq}$ in this series of reactions and just in the investigated range of temperature. The rate of abstraction per active hydrogen may perhaps be 25 or 30 % higher for *p*-xylene or o-xylene than for toluene, *m*-xylene or *m*-fluorotoluene. Such an increase is expected to result from a slight decrease in E by about 0·2 kcal/mole which is less than experimental error of Rebbert's work. Studies of H abstraction by CH_3 radical from toluene, the xylenes and mesitylene by Meyer, Stannett and Szwarc[14] were carried out in liquid phase at 65°C and show a negligible variation in rates per active hydrogen. This result combined with Rebbert's again proves that no appreciable change in activation energy takes place in this series of reactions.

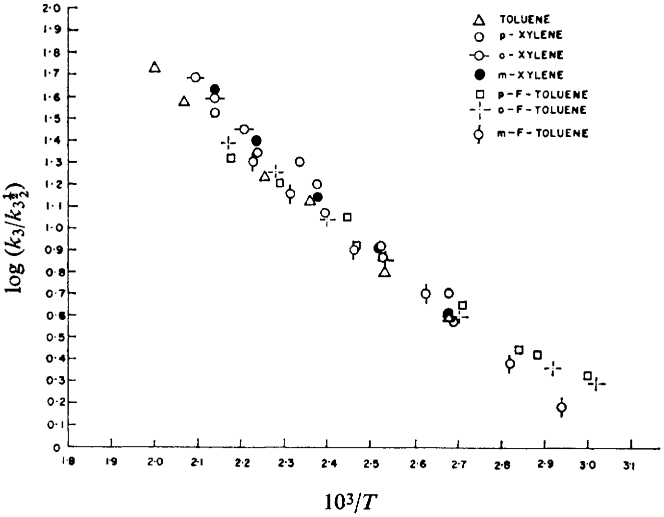


FIG. 3.—An Arrhenius plot for $k_{H,abstr.}/k^{\frac{1}{2}}_{CH_3,comb.}$ (denoted $k_3/k^{\frac{1}{2}}$ in Rebbert's papers). The abstraction takes place from the methyl group of toluene or its derivatives, combination represents the bimolecular combination of methyl radicals into C_2H_6. The values for the xylenes are divided by the statistical factor of 2. The data are taken from Rebbert's papers.[11-13]

Studies of CF_3 radical additions reported by Whittle *et al*[15-17] and by Holmes and Kutschke[18] deserve comment. Calculation of the rate constants by Whittle *et al.* [17] is based on several assumptions. The value of R_{Ad} depends on the method used in computation (I or II), and although the uncertainty caused by this factor is small,[17] it might distort the activation energy by 0·2 kcal/mole. The reaction $A.CF_3+CF_3 \rightarrow A(CF_3)_2$, was not considered by Whittle, although this process seems more probable than the dimerization $CF_3+CF_3 \rightarrow C_2F_6$. This omission may lead to a two-fold error in the rate constant and about 1·5 kcal/mole in the activation energy if the degree of participation of the proposed reaction varies with temperature. The unfortunate choice of experimental conditions could increase such errors; e.g., the rate of photolysis R_{CO} increased with temperature although the amount of reagents remained approximately constant. This leads to a change of the stationary concentrations of the radicals and with rising temperature affects the relative importance of various elementary reactions participating in the overall process. The reversibility of the addition (see above and ref (8)) may be another source of error. This could be an important factor in reactions of fluorinated benzenes, especially in the additions to perfluoro-toluene and xylene. The reversibility of the addition decreases the apparent activation energy, and therefore also lowers the respective A factor. The extremely low A values reported for perfluoro-p-xylene and pentafluoro-toluene could result from this cause.

Although the activation energies reported by Whittle [17] are doubtful, the reported rate constants are probably only slightly in error. For example, the relative values of k_2 reported by Charles, Pearson and Whittle frequently agree within 20-30 % with those reported by Whittemore, Stefani and Szwarc.[3]

In conclusion, the spread in true A values may be not as large as indicated by table 2 of Whittle's paper.[17] The extremely high value of $A_4/A_2^{\frac{1}{2}} = 210\times10^{-8}$ for bromobenzene, given in that table, seems to be in error. Using the data given in table 1 we calculated $E_2-\frac{1}{2}E_1$ to be $4{\cdot}5\pm0{\cdot}5$ kcal/mole, instead of $6{\cdot}7\pm0{\cdot}3$ given in ref. (17), thus leading to a value of only 5×10^{-8} for the respective $A_4/A_2^{\frac{1}{2}}$.

In the series of substrates investigated by Whittle, the A factors need not be constant. (i) His rate constant is a sum of different individual rate constants, e.g., for a mon-substituted benzene the $k_{\text{overall}} = k_p+2k_m+2k_o+k_x$, where k_p, k_m, k_o and k_x represent the rate constants of addition to para-, meta- and ortho-positions and to the position carrying the substituent (see, e.g., ref. (3)). (ii) The structure of the reaction centres vary in his series.

Holmes and Kutschke [18] avoid the problems encountered in calculation of R_{Ad} by using a competitive system. Unfortunately, the formation of C_2F_6 leads to some difficulties. In the calculation of R_{Ad} by means of the equation,

$$R_{Ad} = 2CO—2C_2F_6—CF_3H,$$

it is implied that CF_3 radicals do not interact with radicals such as $CF_3.C_6H_6$, C_6H_5, or C_4H_9, although they dimerize to C_2F_6. This is unjustified. Nevertheless, their results compare well with those of Komazawa, Stefani and Szwarc,[8] who determined $k_{\text{add,benzene}}/k_{\text{abs,DMB}}$ in the gas phase to be 1·23 at 65° and about 1·1 at 150°C, $k_{\text{abs,DMB}}$ denoting the hydrogen abstraction from 2,3-dimethyl butane. Holmes and Kutschke find $k_{\text{add,benzene}}/k_{\text{abs,isobutane}}$ to be 3·5 at 65°C and 3·2 at 150°C. We determined $k_{\text{abs,isobutane}}/k_{\text{abs,DMB}}$ to be 1/3 at 65°C [see appendix] and therefore the agreement between both sets of data is very good. The difference, $E_{\text{add,benzene}} - E_{\text{abs,isobutane}}$, is $-0{\cdot}4$ kcal/mole according to Holmes and Kutschke and $-0{\cdot}3$ kcal/mole according to Komazawa *et al.*[8]

In conclusion, the importance of avoiding side reactions and keeping the system as simple as possible is emphasized. In this respect the system of Holmes and Kutschke is superior to that of Whittle. Whenever the dimerization of primary radicals competes with the investigated elementary process, the possibility of the reaction radical+primary radical→olefin+primary radical—H has to be checked. Although this side reaction is often insignificant, in some processess it may vitiate the experimentally determined activation energy.

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APPENDIX

A discussion with Dr. Kutschke clarified some differences between his and our systems. In his studies[18] the rate of CF_3 formation was a factor 2-3 lower than ours. Unfortunately, his experiments[18] were performed at too low partial pressure of isobutane (P_{IB} = 10-15 mm Hg) and therefore the interaction of CF_3 radicals with other radicals present in the reactor was not eliminated. Now (see above), $P_{DMB} > 500$ mm Hg is required to eliminate this disturbing side process. The problem was further aggravated since at 65°C the reactivity of isobutane towards CF_3 radicals appears to be three times lower than that of 2,3-dimethyl-butane; this value is calculated from an average of 6 experiments performed at 65°C which led to $k_{\text{add,propylene}}/k_{\text{abs,IB}} = 270 \pm 30$.

Another factor makes 2,3-dimethyl-butane a more convenient reagent than isobutane. Disproportionation of radicals formed from these hydrocarbons yields tetramethyl ethylene from DMB and isobutene from isobutane. The ratio $k_{\text{add,tetramethyl ethylene}}/k_{\text{abs,DMB}} \approx 120$ for CF_3 at 65°C, whereas, for the same conditions $k_{\text{add,isobutene}}/k_{\text{abs,IB}} \approx 1000$. Hence, isobutane is eight times more sensitive to contamination by its products of decomposition than is 2,3-dimethyl butane.

In experiments performed at 65°C in 760 mm Hg of DMB we calculated that a complete photolysis of 0·5 mm Hg of hexafluoroazomethane may lead to a maximum loss of 4 % of CF_3 radicals due to the formation of tetramethyl ethylene. Under similar conditions a substantial fraction of CF_3 radicals may be lost in isobutane; our experiments led to the ratio $[CF_3H]/[N_2]$ of 1·75-1·80 indicating a loss of 10-12 % of CF_3 radicals, although *no* C_2F_6 was found in the products.

In spite of these difficulties the agreement between Holmes and Kutschke[18] and Komazawa eg., *et al.*[8] is good, indicating that some losses of CF_3 in Kutschke's system were compensated by CF_3H formation due to the reaction $CF_3+C_6H_6.CF_3 \rightarrow CF_3H+C_6H_5.CF_3$. Further agreement is shown by the results of ten experiments in which hexafluoroazomethane was photolyzed in toluene vapour at 65°C. Although the mole ratio [HFAM]/[toluene] was varied from 1 : 300 to 1 : 70, the ratio $[CF_3H]/[N_2]$ was essentially constant, slightly increasing from $6{\cdot}6 \times 10^{-2}$ to 8×10^{-2}. Since the ratio $[CF_3H/N_2]/[2-CF_3H/N_2]$ determines $k_{\text{abs,toluene}}/k_{\text{add,toluene}}$ a value $0{\cdot}037 \pm 0{\cdot}02$ was found at 65°C. The corresponding value of Holmes and Kutschke[18] is $0{\cdot}06 \pm 0{\cdot}05$ and the value calculated from Whittle's data[15] is 0·07. The ratio of these constants in liquid toluene was[3] 0·036. It is thus relatively easy to obtain concordant results for the rate constants of elementary reactions, but side reactions may considerably distort the activation energies.

[1] Stefani, Herk and Szwarc, *J. Amer. Chem. Soc.*, 1961, **83,** 4732.
[2] Stefani and Szwarc, *J. Amer. Chem. Soc.*, 1962, **84,** 3661.
[3] Whittemore, Stefani and Szwarc, *J. Amer. Chem. Soc.*, 1962, **84,** 3799.
[4] Misra, Stefani and Szwarc, to be published.
[5] Dixon and Szwarc, *Trans. Faraday Soc.*, 1963, **59,** 112.
[6] Dacey and Young, *J. Chem. Physics*, 1955, **23,** 1302.
[7] Pritchard, Pritchard, Schiff and Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52,** 849.
[8] Komazawa, Stefani and Szwarc, *J. Amer. Chem. Soc.*, 1963, **85,** 2043.
[9] Feld and Szwarc, *J. Amer. Chem. Soc.*, 1960, **82,** 3791.
[10] Trotman-Dickenson and Steacie, *J. Chem. Physics*, 1951, **19,** 329.
[11] Burkley and Rebbert, *J. Physic. Chem.*, 1963, **67,** 168.
[12] Sanders and Rebbert, *J. Physic. Chem.*, 1963, **67,** 170.
[13] Wunderlich and Rebbert, *J. Physic. Chem.*, 1963, **67,** 1382.
[14] Meyer, Stannett and Szwarc, *J. Amer. Chem. Soc.*, 1961, **83,** 25.
[15] Charles and Whittle, *Trans. Faraday Soc.*, 1960, **56,** 794.
[16] Charles, Pearson and Whittle, *Trans. Faraday Soc.*, 1961, **57,** 1356.
[17] Charles, Pearson and Whittle, *Trans. Faraday Soc.*, 1963, **59,** 1156.
[18] Holmes and Kutschke, *Trans. Faraday Soc.*, 1962, **58,** 333.