concentration, Fig. 3. It is seen that over a wide concentration range the points fall on a straight line. The intercept at zero concentration gives the portion of the reaction which is catalyzed by the hydronium ions and the water (the uncatalyzed reaction).

A mechanism where the association reaction in equilibrium 2 becomes rate determining at lower pH values, agrees with the observed data of general acid catalysis. The fact that such a proton-transfer reaction is expected to occur in a much shorter time suggests that at lower pH values the rate of the fading reaction is determined by reaction 4 and that this latter reaction is being catalyzed by the buffer.

Acknowledgments.—The author wishes to express his sincere thanks to Dr. S. D. Bailey, Chief of this Laboratory, who helped make this work possible and to John Sousa and Dr. J. Weinstein who helped out on some of the experimental work.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, NEW YORK]

Addition of CF_3 Radicals to Aromatic Hydrocarbons. The Relative Selectivity of CF_3

BY A. P. STEFANI AND M. SZWARC

RECEIVED FEBRUARY 2, 1962

The relative rate constants (k_2) of CF_3 addition to a series of unsubstituted aromatic hydrocarbons were determined. It was shown that a linear relation exists between log (k_2/n) and the atom localization energy of the most reactive center of the hydrocarbon, n being the number of such centers. This indicates the formation of an incipient C-CF_3 bond in the transition state, *i.e.*, in spite of the strongly electrophilic character of CF_3 such a transition state resembles a σ-complex and not a π-complex. The linear plot of $\log(k_2)_{CF_3}$ *versus* $\log(k_2)_{CH_3}$ has a slope 0.8 for the series of investigated hydrocarbons, *i.e.*, benzene, naphthalene, anthracene, etc. This slope is taken as a measure of the intrinsic selectivity of CF_3 radical; its value, lower than unity, shows that the intrinsic reactivity of CF_3 is larger than that of CH_3. The results obtained in this series of unsubstituted aromatic hydrocarbons are compared with those obtained in the series ethylene, propylene and isobutene. The latter reflect the high electrophilic nature of the CF_3 radical and must not be used in determining its intrinsic selectivity. The problem of π- and σ-complexes formed in the addition of a radical to a suitable substrate is discussed. It is suggested that a π-complex is a charge-transfer complex, and its formation does not require activation energy. The formation of σ-complex does require activation energy, this species being the classical adduct radical in which a new σ-bond is formed. Conditions favoring the stability of π-complexes are considered. The significance of such complexes is discussed with reference to the process of formation of σ-complexes.

A method allowing one to determine the relative rate constant of CF_3 radical addition to a series of suitable substrates was described in a preceding paper.[1] The radicals were generated by photolysis of hexafluoroazomethane in iso-octane, their reaction with solvent yielding CF_3H

$$CF_3 + \text{iso-octane} \longrightarrow CF_3H + \text{iso-octyl radical} \quad (1)$$

The addition of a suitable substrate to the solution leads to the reaction

$$CF_3 + \text{substrate} \longrightarrow CF_3.\text{substrate} \quad (2)$$

which competes with (1) for CF_3 radicals. The experimental conditions were such that *all* the CF_3 radicals which escaped "cage" recombination underwent reaction 1 or 2, and none interacted with the radicals formed in the system. Analysis of the products allows calculation of the ratio of the rate constants k_2/k_1, and since k_1 remains constant the data provide information about the relative reactivities of the substrates toward CF_3 radical addition. The results obtained for a series of non-substituted aromatic hydrocarbons are reported in this paper.

Experimental

The experimental technique developed for these studies was described fully in the preceding paper[1] to which the reader is referred for details. A high-pressure mercury lamp (General Electric, AH-6) was used for the irradiation, and since Pyrex glass was employed in the experiments, all light corresponding to $\lambda < 3600$ Å was cut off. The CF_3H/N_2 and C_2F_6/N_2 ratios were determined by gas-chromatography. All the experiments described in this paper were carried out at 65°, and at a constant temperature the C_2F_6/N_2 ratio remained constant. It was demonstrated[1] that "cage" recombination is responsible for the C_2F_6 formation.

The ratio of the rate constants k_2/k_1 was calculated from the equation

$$k_2/k_1 = (X_{HS}/X_A)\cdot\{(CF_3H)/N_{2\text{blank}} - (CF_3H)/N_2\}/\{(CF_3H)/N_2\}$$

where X_{HS} and X_A denote the mole fractions of the solvent and the substrate, $(CF_3H)/N_2$—the ratio of the respective products obtained in an experiment, and $(CF_3H)/N_{2\text{blank}}$ the corresponding ratio observed in the pure solvent, *i.e.*, in the absence of a substrate. The derivation of this equation and its experimental verification is given in reference 1.

The following unsubstituted aromatic hydrocarbons were investigated in the course of this study: benzene, biphenyl, naphthalene, phenanthrene, pyrene and anthracene. Analytically pure benzene was used, and the remaining hydrocarbons were of reagent grade. Each of these compounds was recrystallized several times from a suitable solvent and eventually sublimed in high vacuum. Phenanthrene was first freed from traces of anthracene, by heating its solution with maleic anhydride.[2] The purified compound was then thrice crystallized and vacuum sublimed. The "blue fluorescence" grade anthracene was three times crystallized and then vacuum sublimed.

Spectroscopically pure grade iso-octane was further purified by passing it through a silica-gel column to remove moisture and traces of olefins.

To avoid any photosensitization arising from the light absorption by an aromatic hydrocarbon,[3] a filter consisting of concentrated solution of the investigated hydrocarbon in iso-octane or toluene was introduced between the lamp and the irradiated samples. The calculation indicated that under such conditions more than 99.99% of the light absorbed by the investigated hydrocarbon was removed by the filter.

---

(1) A. P. Stefani, L. Herk and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 4732 (1961).

(2) M. Levy and M. Szwarc, *ibid.*, **77**, 1949 (1955).

(3) See *e.g.*, C. Luner and M. Szwarc, *J. Chem. Phys.*, **23**, 1978 (1955).

TABLE I

ALL THE EXPERIMENTS WERE CARRIED OUT IN ISO-OCTANE AT 65°

k_1 refers to the reaction CF_3 + iso-octane → CF_3H + iso-octyl radical. k_2 refers to the reaction CF_3 + aromatic hydrocarbon → CF_3-(aromatic hydrocarbon)·

Hydrocarbon	Mole %	CF_3H/N_2[a]	k_2/k_1
Benzene	0	1.486 (av. of 3 exp.)	...
	1.09	1.385	6.6
	2.17	1.280	7.2
	5.20	1.042	7.5
	8.40	0.899	7.1
	10.42	0.818	7.0
		Av.	7.1 ± 0.3
Biphenyl	0	0.482 (av. of 3 exp.)	...
	2.13	.365	14.7
	4.26	.288	15.2
	6.39	.242	14.5
	8.52	.200	15.1
	10.65	.171	15.2
		Av.	14.9 ± 0.3
Naphthalene	0	0.271 (av. of 3 exp.)	...
	0.195	.226	101.5
	.391	.192	106.1
	.585	.171	99.9
	.980	.135	103.3
		Av.	102.7 ± 2.6
Phenanthrene	0	0.676 (av. of 3 exp.)	...
	1.25	.293	102.7
	2.47	.196	96.3
	3.68	.144	97.8
	4.85	.112	98.6
	5.96	.093	98.7
		Av.	98.8 ± 2.4
Pyrene	0	0.6765 (av. of 3 exp.)	...
	0.515	.234	365.3
	1.02	.142	363.5
	1.53	.103	360.1
	2.02	.082	350.7
		Av.	359.9 ± 6.5
Anthracene	0	0.745 (av. of 2 exp.)	...
	0.0476	.408	1734
	.0952	.290	1648
	.1430	.238	1493
	.1905	.189	1549
		Av.	1606 ± 107

[a] CF_3H/N_2 is given in arbitrary units which are consistent within each run. See ref. 1.

The irradiation of anthracene solution turned out to be particularly awkward. This hydrocarbon is rapidly photodimerized, and thus it is removed from the filter solution. It was found necessary to change the filter solution every 4 hr. The intensity of transmitted light was low, and consequently, in order to produce a sufficient amount of products, the irradiation had to be continued for 50–60 hr.

Results

The results of all the experiments are collected in Table I. The $(CF_3H)/N_2$ ratios are given in arbitrary units which, however, are self-consistent for each series of experiments.[4] Only in the experiments involving benzene do the $(CF_3H)/N_2$ ratios represent the true molar ratios of the products.

It is important to notice the constancy of k_2/k_1 for any chosen substrate despite a large variation in its concentration. For example, a tenfold increase in the concentration of benzene did not introduce any systematic trend in the respective k_2/k_1's. This observation confirms the proposed mechanism of the reaction which is the basis of our calculations.

Discussion

The results presented in this paper, as well as those reported previously,[1] show that the k_2/k_1 ratios for CF_3 radical addition are substantially greater than those found for the corresponding reactions of methyl radicals. This is shown, *e.g.*, by the data collected in Table II. The abstraction of H atoms by CF_3 radicals is known to proceed faster and to require less activation energy, than abstraction by methyl radicals. The pertinent data may be found, *e.g.*, in a recent note by Pritchard and Miller,[5] who concluded that the differences in the respective activation energies, $E_{CH_3} - E_{CF_3}$, are approximately constant and amount to about 3 kcal./mole. These results are derived on the assumption that the activation energy for CF_3 radical recombination is zero. However, if this recombination requires an activation energy,[6] which is very likely, then the differences $E_{CH_3} - E_{CF_3}$ may be reduced by about 1 or 2 kcal./mole. Nevertheless, even then the unequality $E_{CH_3} > E_{CF_3}$ would remain valid.

TABLE II

$(k_2/k_1)_{CF_3}$ at 65°, $(k_2/k_1)_{CH_3}$ at 85°. Both sets refer to iso-octane as a solvent

Hydrocarbon	$(k_2/k_1)_{CF_3}$	Relative[a] $(k_2/k_1)_{CF_3}/n$	$(k_2/k_1)_{CH_3}$	Relative[a] $(k_2/k_1)_{CH_3}/n$
Benzene	7.1	1.00	~0.4	1.00
Biphenyl	15.9	3.36	2.0	7.50
Naphthalene	102.7	21.7	9	33.0
Phenanthrene	98.8	21.0	11	40.5
Pyrene	359.9	75.8	50	187.5
Anthracene	1606	679	420	2460

[a] n denotes the number of the most reactive centers in the investigated hydrocarbon.

Since the C—H bond dissociation energies in CH_4 and CF_3H are nearly identical,[7,8] it was suggested[7] that the high reactivity of CF_3 radicals in the hydrogen abstraction process should be attributed to their high electronegativity. The greater

---

(4) The technique based on the arbitrary units of the required ratios is more expedient and accurate than that based on their absolute values, for further details see ref. 1.

(5) G. O. Pritchard and G. H. Miller, *J. Chem. Phys.*, **35**, 1135 (1961).

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

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

(8) J. B. Farmer, I. H. S. Henderson, F. P. Lossing and D. J. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

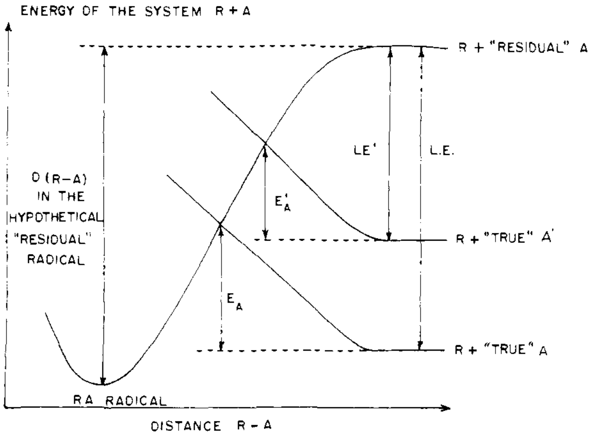

Fig. 1.

electron affinity of CF_3, when compared with CH_3, adds significance to the contribution of the polar structure, $R^+ \ldots H \ldots CF_3^-$, in the transition state. Such a contribution decreases the potential energy barrier of the process and enhances the abstraction. The greatly diminished importance of such a contribution to the transition state of methyl radical abstraction makes the latter less reactive.

Obviously the contribution of polar structures must be even more significant in the transition state of CF_3 addition to olefinic or aromatic compounds, since the exposed π electron cloud of the substrate is more polarizable than the shielded σ electrons of a C–H bond. Hence, the increase in reactivity of the CF_3 radical, compared to that of the methyl, should be much greater for the addition than for the abstraction, making $(k_2/k_1)_{CF_3}$ greater than $(k_2/k_1)_{CH_3}$ as was shown by our observations.

The high reactivity of CF_3 radicals should be reflected in their low selectivity. However, the observations reported in the previous paper[1] seem to contradict this conclusion. It was found that in the series ethylene, propylene and isobutene the $(k_2/k_1)_{CF_3}$ values increase more rapidly than do the respective $(k_2/k_1)_{CH_3}$. The following results were reported[1]: for CF_3 k_2/k_1's increase from 225 to 1720, *i.e.* by a factor of almost 8, whereas an increase by about a factor of only 2 was observed in $(k_2/k_1)_{CH_3}$, namely from 17 to 36. This apparent paradox was explained[1] in terms of the well known electron donating property of methyl substituents. The electrophilic CF_3 radical strongly responds to such an effect, whereas the neutral, or perhaps even slightly nucleophilic, CH_3 is only slightly affected by these substituents. The linear relation between log $(k_2/k_1)_{CF_3}$ and the ionization potential of the respective olefin[1] provided a strong argument favoring this point of view.[9] Therefore, a reliable value for the relative selectivity of CF_3 radicals may be derived only from investigation of their additions to a series of substrates possessing identical reactivity centers with a *constant* electron density. These conditions are probably met in the series of non-substituted aromatic hydrocarbons.

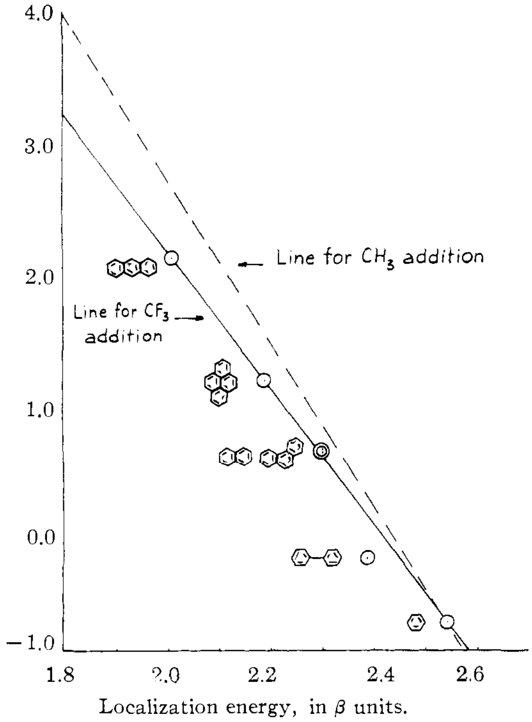

Fig. 2.

It was pointed out[10] that the transition state of a radical addition reaction may be represented by the intersection point shown in the diagram of Fig. 1. Consideration of this diagram led to the conclusion that for a series of substrates possessing the same reaction centers the differences in activation energies for the radical addition reaction are proportional to the respective differences in localization energies. Since the *A* factors (per reactive center) of an addition reaction seem to be approximately constant,[11] a plot of log $(k_2/k_1)/n$ (n being the number of reactive centers) *versus* localization energy should give a straight line. Such a linear relation holds for the addition of methyl radicals to a series of aromatic hydrocarbons,[10] and a similar relation is shown in Fig. 2 for the addition of CF_3 radicals. The dotted line, drawn in Fig 2, for the sake of comparison represents the linear relation for the CH_3 radical addition, and it should be noticed that the slope of the CF_3 line is less steep than that of the CH_3 line.

Since log $(k_2/k_1)_{CF_3}/n$ and log $(k_2/k_1)_{CH_3}/n$ are both linear with respect to localization energy, they must be mutually linearly related (see Fig. 3). It was suggested[10] to refer to the slope of the straight line representing the log of addition of radical R *versus* the log of addition of CH_3 as the relative selectivity α_R of radical R in respect to CH_3. In these terms the relative selectivity of the CF_3 radical is 0.8. Actually even this value may be too high. The increase in the polarizability of condensed aromatic hydrocarbons with their increasing size may

---

(9) In Fig. 1 of ref. 1 an erroneous displacement of the scale shifted the ethylene point to the left. The corrected plot shows a slightly less perfect linear relation between log (k_{CF_3} add/n) and the ionization potential then shown in Fig. 1 of ref. 1.

(10) M. Szwarc, and J. H. Binks, "Theoretical Organic Chemistry" Kekulé Symposium), Butterworth Publ., p. 262 (1959); *J. Chem., Phys.*, **30**, 1494 (1959).

(11) M. Feld and M. Szwarc, *J. Am. Chem. Soc.*, **82**, 3791 (1960).

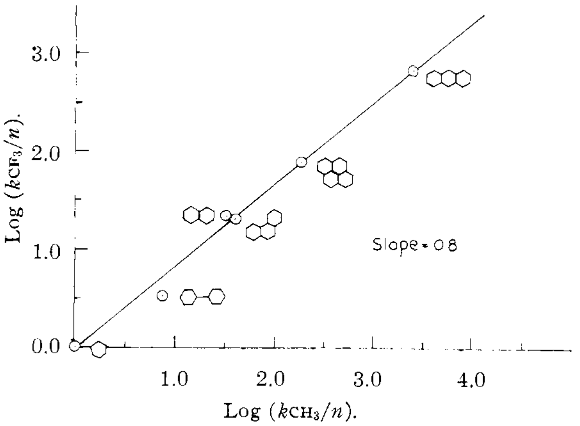

Fig. 3.

result in a steeper rise of the respective $(k_2/k_1)_{CF_3}$ than would be anticipated, and this would lead to an apparently higher value of α_{CF_3}. It is important however, that even thus derived the value of α_{CE_3} is smaller than unity. For the sake of comparison, the relative selectivities of a few other radicals are presented in Table III.[12]

TABLE III

INTRINSIC SELECTIVITIES OF RADICALS

Radical	Relative intrinsic selectivity	Ref.
CH_3	(1)	
C_2H_5	1.0 ($k_{C_2H_5}$ and k_{CH_3} at 65°)	a
n-C_3H_7	1.0 ($k_{C_3H_7}$ and k_{CH_3} at 65°)	b
Iso-C_3H_7	1.0 (?)	c
CF_3	0.8 (k_{CF_3} at 65°, k_{CH_3} at 85°)	d
CCl_3	1.8 (k_{CCl_3} at 90°, k_{CH_3} at 85°)	e
Polystyryl	1.7 (?) ($k_{p\text{-styryl}}$ at 50°, k_{CH_3} at 85°)	f

[a] J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 3322 (1956). [b] J. Smid and M. Szwarc, *ibid.*, **79**, 1534 (1957). [c] J. Smid and M. Szwarc, *J. Chem. phys.*, **29**, 432 (1958). [d] This paper. [e] M. Szwarc, *J. Phys. Chem.*, **61**, 40 (1957). [f] F. Leavitt, V. Stannett and M. Szwarc, *J. Polymer Sci.*, **31**, 193 (1958).

The relative selectivity α_R of the radical R, as defined above, is given by the equation

$$\alpha_R = (1 + \gamma_a^{CH_3}/\gamma_r^{CH_3})/(1 + \gamma_a^R/\gamma_r^R)$$

where $\gamma_a^{CH_3}$ and γ_a^R denote the slopes of the attraction curves, shown in Fig. 1, for CH_3 and R, respectively, while $\gamma_r^{CH_3}$ and γ_r^R are the slopes of the corresponding repulsion curves. The contribution of the polar structure in CF_3 radical addition makes $\gamma_r^{CF_3} < \gamma_r^{CH_3}$ which leads to $\alpha_{CF_3} < 1$ as has been observed; see also F. R. Mays and C. Walling, *Chem. Revs.*, **46**, 256 (1950).

Electrophilic or Nucleophilic Character of the Radical and the Formation of σ or π Complexes.—The effect of polarity on radical reactions was first clearly recognized by Bartlett and Nozaki[13] and by Price.[14] Their ideas were developed further by Walling, Briggs, Wolfstein and Mayo,[15] who amplified and refined Bartlett's concept of the donor–acceptor interaction, and by Alfrey and Price[16] who developed their ingenious Q-e scheme of co-polymerization. Our discussion follows the ideas of Bartlett and Nozaki and of Walling, Briggs, Wolfstein and Mayo.

CF_3 radicals or Cl atoms are much more electrophilic than methyl radicals. Therefore the rates of their addition to, *e.g.*, a C=C double bond, should be more influenced by the presence of electron donating or electron withdrawing substituents than those of methyl radicals. A comparison of CF_3 and CH_3 addition to ethylene, propylene, isobutene and tetrafluoroethylene illustrates this point.[1]

Two distinct products may result from the addition of a radical or a free atom to a suitable substrate: (1) a classical adduct radical, *i.e.*, a species in which a new co-valent bond is formed which links the radical with a particular atom of the substrate; (2) a complex in which the radical and the substrate are held together by forces other than a co-valent bond. Such forces may originate from the expansion of a π orbital of the substrate in the direction of the added species (these are Dewar's π complexes formed with positive ions or electron deficient molecules); they may be due to a charge transfer interaction (Mulliken's charge-transfer complexes); or they may result from other modes of interaction such as dipole–dipole, dipole-induced dipole, etc. In this section we shall be concerned with the formation of charge-transfer complexes (referred to as π-complexes) and their relation to the process of formation of an adduct radical, sometimes referred to as a σ-complex.

Formation of a charge-transfer complex (a π-complex) is facilitated by high electron affinity of the radical and low ionization potential of the substrate. Apparently this process does not require any activation energy (or at least only a very low activation energy) since the range of any repulsive forces is unlikely to be larger than the range of attractive forces resulting from the charge-transfer interaction. The formation of a classic adduct radical (a σ-complex) does require an activation energy, its origin being explained by the diagram shown in Fig. 1.

In a series of reactions in which the same substrate adds different radicals of approximately identical polarity, the activation energy of σ-complex formation is expected to increase as the dissociation energy of the "residual" substrate-radical bond decreases. This relation is anticipated, since the formation of a new σ-bond provides the driving force for the process. Conditions required for justification of such a relation are outlined in Fig. 4. We might expect, therefore, a more rapid formation of a σ-complex on addition of Cl atoms than in the process of addition of Br or I atoms.

The increase in electron-affinity of the radical should enhance the σ-complex formation; this has

---

(12) One of us (M.S.) wishes to correct a statement made in his earlier paper; F. Leavitt, V. Stannett and M. Szwarc, *J. Polymer Sci.*, **31**, 122 (1958). The discussion of the relative selectivity of polystyryl radical led him to the wrong opinion that r_1 determined in the co-polymerization of styrene and vinyl ethyl ether was unreliable. This opinion is not correct, and the deviation observed in the plot log $(1/r_1)$ *versus* log (methyl affinity) probably should be attributed to polar factors.

(13) P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **68**, 1495 (946).

(14) C. C. Price, *J. Polymer Sci.*, **1**, 83 (1946).

(15) C. Walling, E. R. Briggs, K. B. Wolfstein and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1537 (1948).

(16) T. Alfrey and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).

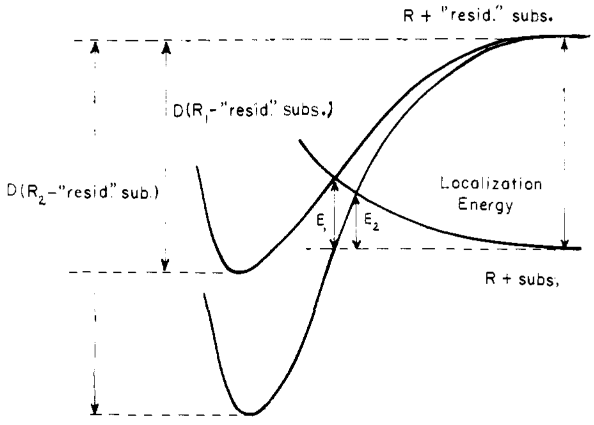

Fig. 4.—This is a modified diagram of Fig. 1, illustrating the interaction of two radicals of the same polarity forming bonds of different strength with the substrate. It is assumed that the repulsion curve remains the same for both radicals, but the increasing strength of the bond makes one attraction curve steeper than the other. This leads to a decrease in the activation energy of the process.

been previously explained in terms of the contribution of a polar structure to the transition state. However, if the hump in potential energy is sufficiently high and the electron-affinity of the radical sufficiently large, then a dip may develop in the potential energy surface as shown in Fig. 5. Under such conditions a relatively stable π-complex would be formed before a σ-complex is produced.

Formation of a π-complex may hamper the ultimate formation of a σ-complex. This does not mean that the high electron-affinity of the attacking radical inhibits the formation of a σ-complex. On the contrary, as has been pointed out, this enhances the addition reaction and lowers its potential energy barrier. However, if the dip corresponding to a π-complex is deeper than the decrease in the potential energy barrier of a σ-complex formation process, the system becomes stabilized by the formation of a π-complex. A similar line of argument has been used by Walling and Mayahi[17] in their discussion of solvent effects.

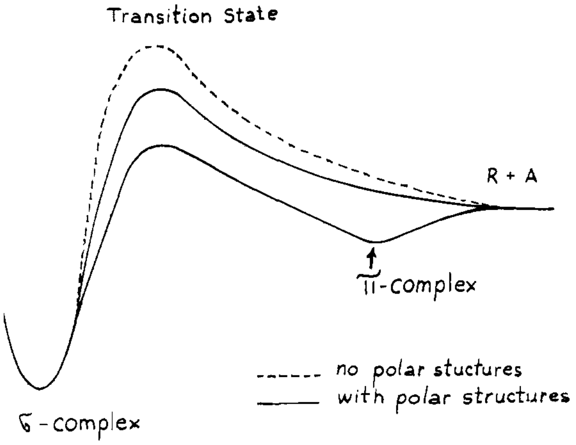

Fig. 5.

The existence of π-complexes in reactions of radicals and free atoms is demonstrated by several observations. The effect of solvents upon the rates of radical reactions, and in particular upon the rates of Cl atom abstraction reactions, provides an important evidence for the existence of π-complexes. For example, Russell[18] has shown that such solvent effects do not correlate with the rates of addition of phenyl or methyl radicals to these solvents (benzene and other aromatics), but they may be correlated with their basicities. This indicates that in aromatic solvents Cl atoms form π-complexes, and this affects their reactivities and hinders their addition to these solvents. An even more striking evidence for π-complex formation was provided by the recent work of Abell and Piette.[19] These workers succeeded in observing the electron spin resonance (e.s.r.) spectra of radicals produced by the addition of Br atoms to some olefins at −80°. The structure of the spectra proves that the Br atom adds to the middle of the C=C bond indicating, in our opinion, the formation of a π-complex. In our interpretation, the low temperature and low C–Br bond dissociation energy prevents (or slows down) the process

$$\pi\text{-complex} \longrightarrow \sigma\text{-complex}$$

and hence the π-complex accumulates in the system. Moreover, since the recombination of π-complexes is probably slower than that of ordinary radicals (*i.e.*, σ-complexes), their stationary concentration is higher, providing convenient conditions for e.s.r. studies. The formation of π-complexes resulting from the addition of O atoms to olefins is discussed by Cvetanovic.[20] He assumes that such an addition requires a substantial activation energy (see Fig. 6) and that the resulting π-complex is separated from the ultimate σ-complex by a lower potential energy barrier. Thus, the formation of the π-complex is, in his opinion, the rate determining step in the σ-complex formation.

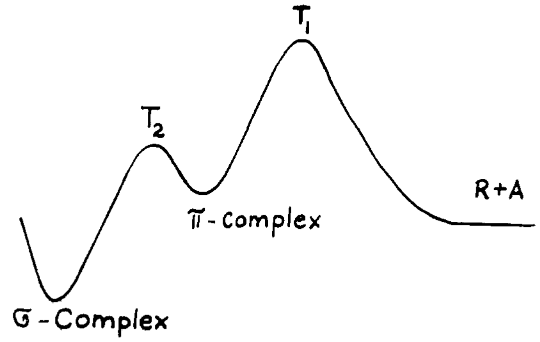

Fig. 6.

We raise two objections to this representation: (1) There is no valid reason to expect a high potential energy barrier in π-complex formation. (2) If such a barrier does exist, then it is superfluous to consider a lower hump separating the π- and σ-complexes. The system would acquire the

---

[17] C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

[18] G. A. Russell, *ibid.*, **80**, 4987 (1958).

[19] P. I. Abell and L. H. Piette, Fifth Intern. Symp. on Free Radicals (1961).

[20] R. J. Cvetanovic, *Can. J. Chem.*, **38**, 1678 (1960); see also *J. Chem. Phys.*, **30**, 19 (1959); and G. Boocock and R. J. Cvetanovic, *Can. J. Chem.*, **39**, 2436 (1961).

necessary excess of energy in passing the first hump, and conceptually the second hump would only be of significance if a mechanism existed to dissipate the internal energy of the complex before it reached its final σ-state. In the radical or free atom addition it is doubtful whether such a mechanism does exist.

One point, however, needs further discussion. If both π- and σ-complexes are feasible, does the transition state resemble a π- or a σ-complex? The transition state under consideration is the one described by the hump separating the π- and σ-complexes and not by a hump preceding the π-complex (if such a hump exists at all). Our studies of the addition of CF_3 radicals to unsubstituted aromatic hydrocarbons indicate that the transition state for this reaction resembles a σ-complex, *i.e.* even for this strongly electrophilic radical an incipient C–CF_3 bond is formed in the transition state. The addition of O-atoms may follow a different course, and, if this is the case, we suggest that the di-radical nature of O-atoms, and not their electrophilic character, may be responsible for such behavior.

The following point needs, however, further discussion. If both π- and σ-complexes are feasible, does the transition state resemble a π- or a σ-complex? The transition state under consideration is the one described by the hump separating the π - and σ-complexes and not by a hump preceding the π-complex (if such a hump exists at all). The addition of CF_3 radicals to benzene and some of its derivatives was studied recently by Whittle, *et al.*[21] and their findings suggest that a covalent C–C bond is formed in this process. The results of our studies permit us to go further and claim that the incipient C–C bond is formed in the transition state since the respective rate constants per reactive center were found to be related to the respective localization energies. This means that even for this strongly electrophilic radical the transition state resembles a σ- and not a π-complex. The addition of O-atoms may follow a different course, and, if this is the case, we suggest that the di-radical nature of O-atoms, and not their electrophilic character, may be responsible for such a behavior.

In conclusion we wish to emphasize that the electrophilic nature of a radical is reflected in its response to the presence of electron-donating or electron-withdrawing substituents in the substrate. Such a response is observed whether the addition leads directly to a σ-complex or proceeds *via* a π-complex. The electrophilic character of a radical might favor the formation of a π-complex, although such a complex need not necessarily be formed in every addition involving an electrophilic radical. Whenever a π- and σ-complex are formed in the same process, the formation of the former cannot be the rate determining step in the formation of the latter.

The transition state of the addition of a strongly electrophilic CF_3 radical to aromatic or olefinic substrates resembles a σ-complex. Relatively stable π-complexes probably are formed with extremely electrophilic radicals or free atoms. They are favored by reactions leading to relatively weak σ-bonds in the final adduct radical and by low temperature. The adducts observed by Abell and Piette are probably π-complexes.

We wish to acknowledge the financial support of this work by Wright Air Development Division, Contract AF33(616)7662 and by the National Science Foundation. We also wish to thank Dr. F. R. Mayo for reading the manuscript and for his constructive suggestions.

---

[21] S. W. Chailes and E. Whittle, *Trans. Faraday Soc.*, **56**, 794 (1960); S. W. Chailes, J. T. Pearson and E. Whiffle, *ibid.*, **57**, 1356 (1961).

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN]

High-resolution Fluorine Magnetic Resonance Spectra of Some Perfluoroalkyl Derivatives of Sulfur Hexafluoride[1]

BY MAX T. ROGERS AND JOHN D. GRAHAM[2,3]

RECEIVED MARCH 19, 1962

The high-resolution fluorine magnetic resonance spectra of a group of perfluoroalkyl derivatives of sulfur hexafluoride have been analyzed and the chemical shifts and spin–spin coupling constants determined. The fluorine chemical shifts are found to vary with the electronegativity of the substituents. Fluorine–fluorine coupling constants are observed between nuclei separated by three, four and five bonds, but the coupling constants do not vary in a coherent manner with a change in the number of bonds separating interacting nuclei. Our results are in agreement with the idea that coupling between fluorine nuclei separated by three or four single bonds is due to both through-space and through-bond interactions but that the importance of the through-bond interaction falls off rapidly with number of intervening bonds and the coupling is largely a through-space interaction when the nuclei are separated by five single bonds. The very small coupling constants observed for interaction between nuclei separated by three bonds in the CF_3–CF_2 and –CF_2–CF_2– fragments would still appear to be anomalies possibly to be explained as resulting from rotational averaging of *trans* and *gauche* coupling constants of opposite signs.

Introduction

Although fluorine magnetic resonance spectra for a number of fluorocarbon derivatives have been studied, much less systematic data for F^{19} chemical shifts and spin–spin coupling constants exist than

---

(1) This research was supported by a grant from the Atomic Energy Commission.

(2) Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut.

(3) Taken in part from the Ph.D. thesis of John D. Graham, Michigan State University, 1961.