JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 84 OCTOBER 31, 1962 NUMBER 20

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE RADIATION LABORATORY, CONTINENTAL OIL COMPANY, PONCA CITY, OKLAHOMA]

Free Radical Reactions Initiated by Ionizing Radiation. II. Rate Constants for Hydrogen Atom Addition Reactions with Mono-olefins, Butadiene and Benzene

BY KANG YANG

RECEIVED APRIL 2, 1962

Various olefins reduce the rate of formation of hydrogen in the gamma radiolysis of propane. The effect of temperature on this inhibition strongly indicates that it results from the hydrogen atom addition reaction H + olefin $\xrightarrow{k_s}$ H-olefin. Rate constants k_s for these addition reactions are determined here for the compounds: butadiene-1,3, isobutene, tetramethylethylene, *trans*- and *cis*-butene-2, and benzene. These data together with the results of Part I are used to pursue correlations between activation energies (but not log k_s) and reactivity indices computed by a simple molecular orbital theory. It is found that $\epsilon = aE_{loc} - b$, where ϵ denotes activation energy, E_{loc} signifies localization energy, and a and b are constants. Free valency fails to give a similar linear relation.

Introduction

The reactivities of conjugated molecules in free radical addition reactions played an important role in testing current molecular orbital theories of chemical reactivity.[1-4] In these reactions the main factor governing relative rates seems to be the energy change that occurs in loosely bound π-electrons as attacking free radicals approach reaction centers. This energy change in π-electron systems can be expressed approximately in terms of various reactivity indices which are often found to correlate linearly with log k_s, where k_s signifies a rate constant determined at a single temperature in a series of similar reactions. This linearity is then interpreted to mean that the activation energies for these reactions and the reactivity indices of the reactants are themselves linearly related and that, aside from symmetry change, the pre-exponential factors are approximately the same. This quite reasonable explanation seems to break down in the case of the methyl radical addition reactions with mono-olefins in solutions.[5] In that case, differences in pre-exponential factors seem to determine relative rates even if there exist correlations between reactivity indices and log k_s.[3] In view of this and also considering the fact that reactivity indices indicate an energy change but not an entropy change, it is highly desirable to investigate direct relations between reactivity indices and activation energies. Successful attempts to do this seem to be absent from the literature, probably because of experimental difficulties encountered in estimating activation energies accurately.

The present paper attempts to demonstrate this direct correlation. The hydrogen atom addition reactions with olefins in the gas phase are well suited for the purpose because here solvation effects are absent and undesirable steric hindrances are minimized.[6] Accuracy of activation energy data critically depends on the investigated temperature ranges.[7] Results given in Part I of the present series[8] (hereafter denoted as Part I) indicate that, if gamma radiation is used to generate hydrogen atoms from propane, reaction temperatures can be changed widely (50–150°).

The second object of the present paper is to consolidate new experimental methods[9-11] for

---

(1) C. A. Coulson, *J. Chem. Soc.*, 1435 (1955).

(2) M. Szwarc, *J. Phys. Chem.*, **61**, 40 (1957).

(3) S. Sato and R. J. Cvetanovic, *J. Am. Chem. Soc.*, **81**, 3223 (1959).

(4) For a recent review, see R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959.

(5) R. P. Buckely and M. Szwarc, *Proc. Roy. Soc.* (London), **A240**, 396 (1957).

(6) K. R. Jennings and R. J. Cvetanovic, *J. Chem. Phys.*, **35**, 1233 (1961).

(7) For example, see S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 91–92.

(8) K. Yang, *J. Am. Chem. Soc.*, **84**, 719 (1962).

(9) R. A. Back, *J. Phys. Chem.*, **64**, 124 (1960).

utilizing gamma radiation in the investigation of free radical kinetics. These methods utilize the observation that unsaturated compounds (S) often reduce the yield of hydrogen in the radiolysis of saturated hydrocarbons (M).[12] A radical mechanism for this inhibition is

$$\mathrm{M} \rightsquigarrow \mathrm{H} \qquad (1)$$

$$\mathrm{M} \rightsquigarrow \mathrm{H_2} \qquad (2)$$

$$\mathrm{H} + \mathrm{M} \xrightarrow{k_\mathrm{m}} \mathrm{H_2} + \mathrm{R} \qquad (3)$$

$$\mathrm{H} + \mathrm{S} \xrightarrow{k_s} \mathrm{H\text{-}S} \qquad (4)$$

$$\mathrm{H} + \mathrm{S} \xrightarrow{k'_s} \mathrm{H_2} + \mathrm{R'} \qquad (5)$$

It can be shown that[13,14]

$$(r_0 + r_s)^{-1} = (1/r_1)(k_\mathrm{m}/k_s)([\mathrm{M}]/[\mathrm{S}]) + (1/r_1)(1 + k'_s/k_s) \qquad \text{(E-1)}$$

where r_0 and r_s denote, respectively, the rate of formation of hydrogen in the absence and presence of S; and r_1 is the rate of reaction 1.

Recent publications point out that with (E-1) alone the proposed radical mechanism cannot be demonstrated because the same form of rate equations results whether S is assumed to react with electrons, positive ions, neutral molecules or free radicals.[15-18] In addition, apparent linearity of a plot of $(r_0 - r_s)^{-1}$ *versus* [M]/[S] in a narrow range of S does not provide an unambiguous test of (E-1).[18]

There is, however, another relation

$$\log k_\mathrm{m}/k_s = - \beta/T \qquad \text{(E-2)}$$

where α and β are constants, which reproduces the variation of inhibition with temperature within experimental accuracy in all of the systems of present concern. The form of (E-2) together with the magnitudes and trends of α and β is such that the possibility that S reacts with species other than hydrogen atoms is quite remote; hence we presume that, for those systems in which both (E-1) and (E-2) are applicable, the above radical reactions correctly represent the inhibition mechanism. It follows, then, that α and β in (E-2) signify, respectively, log of the relative pre-exponential factor and difference in activation energies for reactions 3 and 4.

Experimental

All hydrocarbons except tetramethylethylene were Phillips research grade. These were degassed and distilled as described previously.[8] Tetramethylethylene (an A.P.I. standard purchased from the Carnegie Institute of Technology, Pittsburgh, Pennsylvania) was degassed and used without the distillation. Propane was used as a hydrogen atom source, and all rate data were obtained at very low conversions ($\sim 10^{13}$ per cent.) to avoid possible errors arising from secondary reactions.

Two types of Pyrex reactors, both of 140 cc., were used. One type had a capillary constriction and a break-off seal. The other type was equipped with a capillary neck at the end of which a stopcock was attached. The former could be used only once, while the latter could be used repeatedly. Both types gave the same results, and most of the data were obtained using the latter type. The energy input rate, from 1 × 10^4 curies of $\mathrm{Co^{60}}$, was 1.3 × 10^{-3} ev. per hour per molecule of propane. Other experimental details have been described previously.[8]

Results

Table I summarizes typical experimental results showing decrease in the rate, $[\mathrm{H_2}]/[\mathrm{C_3H_8}]$ per hour, at 193° with increasing isobutene concentration. A plot of these data according to (E-1) gives a good straight line

$$(r_0 - r_s)^{-1} = (42.1 \pm 1.8)[\text{isobutene}]/[\text{propane}] + (1.7 \pm 0.1) \times 10^4 \qquad \text{(E-3)}$$

where error ranges are indicated in terms of standard deviations resulting from least squares treatment. The rate r_1 of hydrogen atom production is determined to be 6.23×10^{-5} by using ethylene in which $k'_s = 0$. This r_1 together with (E-2) and (E-3) gives

$$k_\mathrm{m}/k_s = 2.62 \times 10^{-3} \text{ and } k'_s/k_s = 0.06$$

Because of uncertainties in the intercepts of the (E-1) plots, estimations of k'_s/k_s often varied over 100%. For this reason, no attempt is made to report k'_s/k_s.

TABLE I

HYDROGEN FORMATION IN THE RADIOLYSIS OF PROPANE-ISOBUTENE SYSTEMS AT 193°

$[\mathrm{C_3H_8}]$,[a] mm.	$[i\text{-}\mathrm{C_4H_{10}}]/[\mathrm{C_3H_8}]$ × 100	Irrad. time,[b] min.	$[\mathrm{H_2}]/[\mathrm{C_3H_8}]$ × 10^5	Rate[c] × 10^5
501	0.000	20	2.77	8.31
501	.235	30	2.74	5.48
501	.353	30	2.38	4.76
501	.471	30	2.24	4.48
501	.706	30	1.97	3.94
501	1.41	30	1.68	3.36

[a] Pressure at room temperature. [b] Energy input rate = 1.3 × 10^{-3} ev. per hour per molecule of propane. [c] $[\mathrm{H_2}]/[\mathrm{C_3H_8}]$ per hour.

Figure 1 summarizes the effect of temperature variations on k_m/k_s for various olefins. The resulting straight lines are in good agreement with (E-2). All of the data were subjected to least squares treatment, and rate constant parameters thus obtained are given in Table II.

TABLE II

RATE CONSTANT k_s ($= BT^{1/2}e^{-\epsilon/RT}$) FOR THE ADDITION REACTIONS H + S → HS, RELATIVE TO THE RATE CONSTANT k_m FOR THE ABSTRACTION REACTION $\mathrm{H} + \mathrm{C_3H_8} \rightarrow \mathrm{H_2} + \mathrm{C_3H_7}$

S	log (B_m/B_s)	$\epsilon_\mathrm{m} - \epsilon_s$ (kcal./mole)
Butadiene-1,3	0.21 ± 0.50	6.5 ± 1.0
Isobutene	.23 ± .13	6.2 ± 1.1
Tetramethylethylene	.39 ± .15	5.2 ± 0.3
trans-Butene-2	− .33 ± .07	3.5 ± .3
cis-Butene-2	− .31 ± .12	3.5 ± .1
Benzene	.39 ± .15	3.5 ± .3

Discussion

Comparison with Previous Investigations.—As for the temperature effects reported here, there seem

---

(10) T. J. Hardwick, *J. Phys. Chem.*, **65**, 101 (1961); **66**, 291 (1962).

(11) K. Yang and P. L. Gant, *ibid.*, **65**, 1861 (1961).

(12) For example, see L. M. Dorfman, *ibid.*, **62**, 29 (1958).

(13) For example, see ref. 10.

(14) When $k'_s \ll k_s$, (E-1) takes a simpler and convenient form used in Part I.[8] In the present experiments, k'_s/k_s often exceeded 0.1, which necessitated the use of (E-1).

(15) J. H. Baxendale and F. W. Mellows, *J. Am. Chem. Soc.*, **83**, 4720 (1961).

(16) J. M. Ramaradhya and G. R. Freeman, *Can. J. Chem.*, **39**, 1769 (1961).

(17) J. M. Ramaradhya and G. R. Freeman, *ibid.*, **39**, 1843 (1961).

(18) P. J. Dyne and W. M. Jenkinson, *ibid.*, **39**, 2163 (1961).

to be no comparable data in the literature. At a single temperature, 23.5°, however, the data in Table II can be compared with recent results obtained by investigating hydrogen formation in the photolysis of *n*-butane–olefin systems.[6] These are given in Table III where k_p for the addition reaction to propylene is taken as 2.9×10^{11} cc./mole sec., this value being estimated from (E-4) to be given below. The two sets of data are in reasonable agreement.

TABLE III

RATES FOR THE HYDROGEN ATOM ADDITION REACTIONS WITH VARIOUS OLEFINS AT 23.5°

S	k_s (cc./mole sec.) $\times 10^{-11}$ Ref. 6	This work
Butadiene-1,3	14.0	37.7
Isobutylene	7.2	27.6
Tetramethylethylene	2.4	3.2
Propylene	2.9	2.9
Ethylene	1.6	1.9
trans-Butene-2	1.7	1.0
cis-Butene-2	1.4	0.9
Benzene	..	0.1

Absolute Rate Constants.—In Part I, the activation energy E_p for the addition reaction with propylene is assumed to be 1.5 kcal. per mole. This value was taken from the investigation of the addition reaction with solid propylene in the temperature range of 77–90°K.[19] The present results demand a slightly higher E_p; otherwise the activation energy of the addition reaction to butadiene becomes too low (−0.1 kcal.). It is not unreasonable to use a higher value, since E estimated as $E = -R\partial(\ln k)/\partial(1/T)$, may depend slightly on temperature as is the case with collision theory rate constants

$$k = BT^{1/2}\exp(-\epsilon/RT) \text{ and } -R\partial(\ln k)/\partial(1/T) = \epsilon + (1/2)RT$$

Some published values for E_p and ϵ_p are listed in Table IV.[20–22] The apparent tendency for E_p to increase with increasing reaction temperature should not be taken seriously because error ranges in these data are now known. The average of these ϵ_p values, 2.2 kcal. per mole, seems to be reasonable and was used here. In Part I, arguments were given for preferring a k_p value of 4.8×10^{11} cc./mole sec. at 31°; then

TABLE IV

ACTIVATION ENERGY FOR THE HYDROGEN ATOM ADDITION REACTION WITH PROPYLENE

Temp., °K.	E, kcal./mole	ϵ,[a] kcal./mole	Ref.
77– 90	1.5	1.3	19
304	1.8	1.2[b]	20
304	2.6	2.0[b]	21
298–388	5.0	4.2	22

[a] $\epsilon = E - 0.5\,R\langle T\rangle$, where $\langle T\rangle$ is the average of the highest and lowest reaction temperature. [b] These values are obtained assuming a steric factor of 10^{-2}.

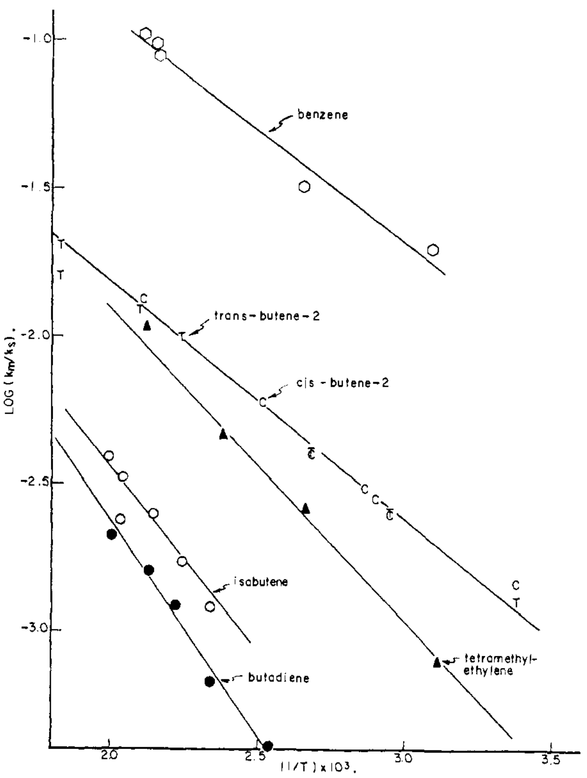

Fig. 1.—Variation of rate constants with temperature for the hydrogen atom addition reactions with various olefins.

$$k_p = 10^{12.0}T^{1/2}\exp(-2.2 \times 10^3/RT) \qquad \text{(E-4)}$$

Re-evaluation of data in Part I gives

$$k_m = 10^{12.2}\,T^{1/2}\exp(7.0 \times 10^3/RT)$$

Here, k_m is a composite rate constant for the reaction of hydrogen atoms with propane producing both primary and secondary propyl radicals. Absolute rate constants obtained in this way are summarized in Table V where the results in Part I are also included for comparison.

TABLE V[a]

RATE CONSTANTS, k_s (CC./MOLE SEC.), FOR THE HYDROGEN ATOM ADDITION REACTIONS WITH VARIOUS OLEFINS, S

$$\log k = \log B - \frac{\epsilon}{4.58 \times 10^{-3}\,T} + 0.5 \log T$$

S	B_s	ϵ_s
Butadiene-1,3	12.0	0.5
Isobutene	12.0	0.8
Tetramethylethylene	11.8	1.8
Propylene	12.0	2.2
Ethylene	12.1	2.6
trans-Butene-2	12.5	3.5
cis-Butene-2	12.5	3.5
Benzene	11.6	3.5

[a] For the reaction, $H + C_3H_8 \xrightarrow{k_m} H_2 + C_3H_7$, $\log k_m = 12.2 - (7.0)/(4.58 \times 10^{-3}\,T) + 0.5 \log T$.

Before discussing the ϵ values in Table V in terms of reactivity indices, one point is worth noting. Isobutene reacts much more readily

---

(19) M. D. Scheer and R. Klein, *J. Phys. Chem.*, **65**, 375 (1961).

(20) H. W. Melville and J. C. Robb, *Proc. Roy. Soc.* (London), **A196**, 494 (1949).

(21) A. B. Callear and J. C. Robb, *Trans. Faraday Soc.*, **51**, 638 (1955).

(22) B. de B. Darwent and R. Roberts, *Discussions Faraday Soc.*, **14**, 55 (1953).

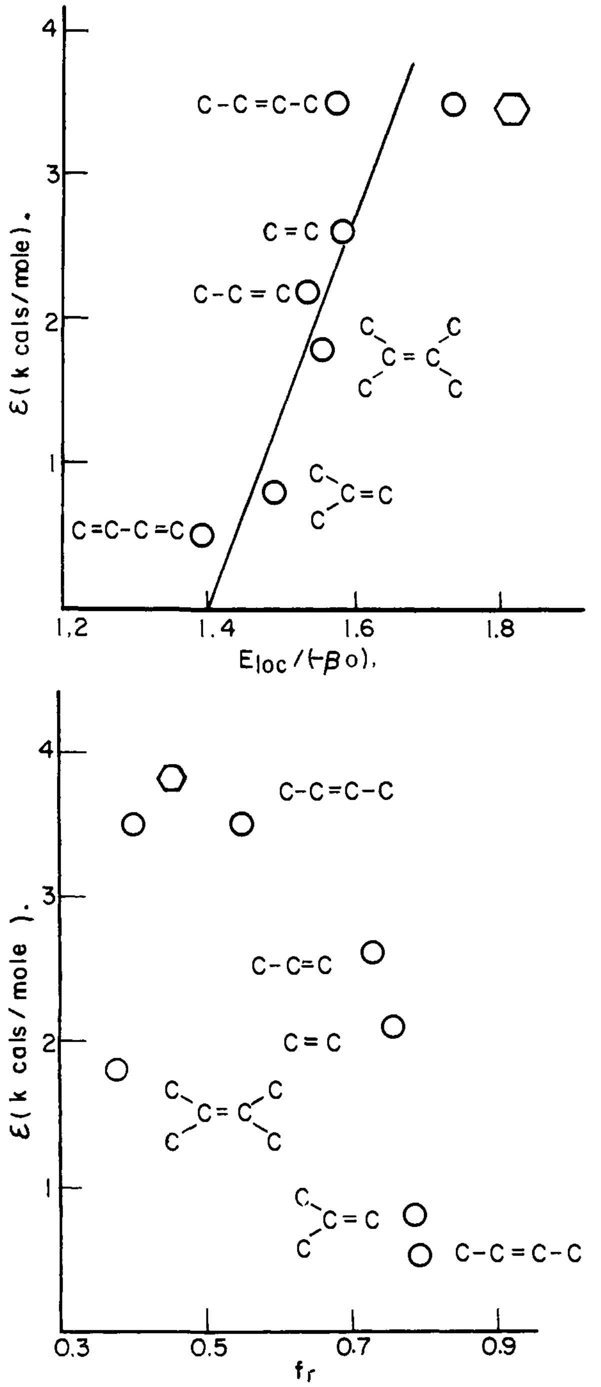

Fig. 2.—(A) (top) Activation energy *versus* localization energy. (B) (bottom) Activation energy *versus* free valency.

than butene-2

$$k(\text{butene-2})/k(\text{isobutene}) = 10^{-0.4}\exp(-0.9 \times 10^3/RT) \quad \text{(E-5)}$$

Both theoretical and experimental results[3] indicate that this is so if the attacking species are radicals but not so if they are ions; hence (E-5) can be used to differentiate radical precursors from ionic ones in the formation of hydrogen molecules. Elucidation of various radiolysis mechanisms often demands this differentiation.

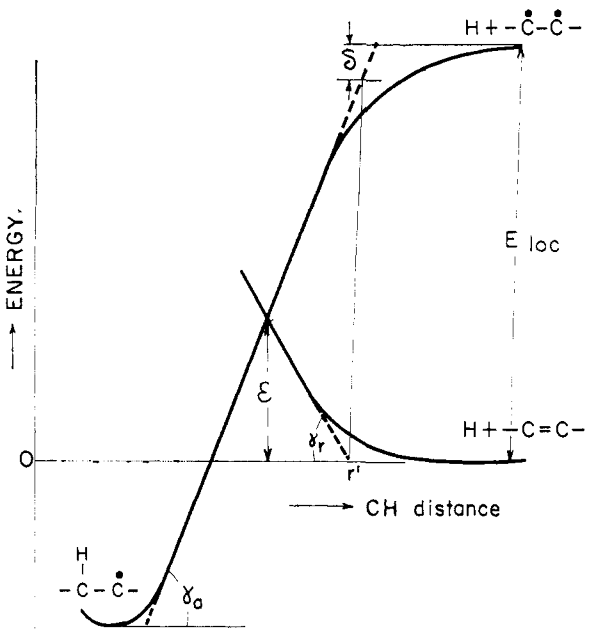

Fig. 3.—A simple potential model for addition reactions.

Activation Energies and Reactivity Indices.—Two reactivity indices of frequent use are localization energy (E_{loc})[23] and free valency (f_r).[24] In the present case, E_{loc} is an energy required for localizing a π-electron at a reaction center; f_r is a quantity related to an energy change in π-electronic systems as a result of a small perturbation at a reaction center. While f_r relates to the initial stage of a reaction, the concept of E_{loc} stresses the importance of the final stage. When overlap integrals are included and a hyperconjugation effect is present, these two different views often lead to substantially different estimates of relative reactivities.[4]

Localization energy in benzene was computed by using parameters given by Lofthus.[25] He lists two sets of parameters, one using Slater orbitals and the other using SCF (self consistent field) orbitals. The use of the former gives $E_{loc} = -1.73\ \beta_0$, where β_0 signifies the resonance integral for a C–C distance of 1.543 Å. minus overlap times coulomb integral. Other reactivity indices were taken from a paper by Sato and Cvetanovic[3] who employed the same parameters.

Figure 2A compares ε and E_{loc}, while Fig. 2B compares ε and f_r. Here, only those carbon atoms having the highest reactivity in each molecule are considered. Relative activation energies predicted by f_r are incompatible with the present results. Least squares treatment of the data in Fig. 2A according to a linear relation

$$\epsilon(\text{kcal./mole}) = aE/(-\beta_0) + b \quad \text{(E-6)}$$

gives these values for two constants a and b

$$a = 10 \pm 3,\ b = 13 \pm 4$$

---

[23] G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

[24] N. V. Swartholom, *Arkiv Kemi, Mineral. Geol.*, **15A**, No. 3 (1941); R. Daudel and A. Pullman, *Compt. rend.*, **220**, 888 (1945); C. A. Coulson, *Trans. Faraday Soc.*, **42**, 106, 265 (1946).

[25] Lofthus, *J. Am. Chem. Soc.*, **79**, 24 (1957).

In view of possible uncertainties in both the theory and the experiment, the standard deviations in a and b may be considered to be reasonable; and this conclusion can be drawn: The activation energies increase linearly with increasing localization energies.

An interesting fact here is the presence of term b in (E-6) which seems not to have been reported before. A qualitative explanation of b can be obtained by considering a simple but useful model representing potential changes in the addition reaction given by Szwarc[2] and by Binks and Szwarc.[26] The essence of this model is depicted in Fig. 3. Here, r' is a C–H distance at which the potential of hypothetical straight line repulsion becomes equal to the potential of the reactants; δ is the difference between E_{loc} and the potential of hypothetical straight line attraction at r'. Meanings of the other symbols and various assumptions involved in this model are discussed in the original references.[3,26] Simple geometric considerations give these relations

$$a = \left(1 + \frac{\tan \gamma_a}{\tan \gamma_r}\right)^{-1} \qquad \text{(E-7)}$$

and

$$b = a\delta \qquad \text{(E-8)}$$

Binks and Szwarc suggested that, in a series of similar reactions, γ_a and γ_r are approximately constant. If so, r' and the related δ are likely to stay constant also. This would explain why ϵ increases linearly with increasing E_{loc} as shown in (E-6).

Acknowledgments.—We express our appreciation to Dr. F. H. Dickey, Dr. L. O. Morgan and Mr. C. L. Hassel for their valuable discussion and Mr. J. D. Reedy for helping with the experimental work.

---

(26) J. H. Binks and M. Szwarc, *J. Chem. Phys.*, **30**, 1494 (1959).

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

Addition of CF_3 Radicals to Substituted Benzenes

BY I. M. WHITTEMORE, A. P. STEFANI AND M. SZWARC

RECEIVED APRIL 28, 1962

The relative rate constants of addition of CF_3 radicals to substituted benzenes have been determined. Electron donating groups such as $-CH_3$ or $-OCH_3$ enhance the reaction, while electron withdrawing groups such as $-CF_3$, $-CN$, etc., slow it down. Halogenated benzenes are slightly less reactive than benzene, iodobenzene being an exception. The low reactivities of *t*-butylbenzene and *p*-di-*t*-butylbenzene are attributed to shielding of the ortho positions by the bulky *t*-butyl groups. The relative rates of CF_3 radicals addition show poor correlation with Hammett's σ factors. This is anticipated, since each of the measured relative rate constants, k_2, is the sum of the rate constant for all positions, *i.e.*, $k_2 = k_p + 2k_m + 2k_o + k_x$. In spite of this, an unexpectedly good correlation was shown with the ionization potential of the substrate. The relative rate constants of H-atom abstraction have been determined for toluene, mesitylene, ethylbenzene and cumene. These data are compared with those obtained for methyl radicals. It appears that the more reactive CF_3 radicals are more selective. This anomaly calls for further studies. Finally, the effect of solvent upon the cage recombination of CF_3 radicals is discussed.

In an earlier paper[1] we described a technique which allowed us to determine the relative rate constants of CF_3 radical addition to unsaturated and aromatic substrates. The radicals were produced by the photolysis of hexafluoro-azomethane in isoöctane solution, and in the absence of a suitable substrate, all the CF_3 radicals which escaped the cage recombination yielded CF_3H through reaction 1

$$CF_3 + \text{isoöctane} \longrightarrow CF_3H + \text{isoöctyl radical} \qquad (1)$$

In the presence of a substrate A, to which radicals may add reaction 2 ensues and the latter competes

$$CF_3 + A \longrightarrow CF_3A\cdot \qquad (2)$$

with (1) for CF_3 radicals causing a decrease in the yield of CF_3H as the concentration of A increases. From the magnitude of this decrease the ratio of the rate constants k_2/k_1 was calculated. The details of the experimental technique, the proof of the suggested kinetic scheme and the verification of the equation that gives the k_2/k_1 ratio are reported in ref. 1 and will not be repeated in this paper.

The above method was used recently to determine the k_2/k_1 ratios for a series of non-substituted polynuclear aromatic hydrocarbons,[2] and now it has been applied to a series of substituted benzenes, in order to determine the effect of substituents upon the value of k_2/k_1.

The addition of a radical to substituted benzene may take place in the position *para*, *meta*, or *ortho* to the investigated substituent, and it may also take place on the carbon atom bearing the substituent X. Hence, the measured rate constant k_2 is a sum, *i.e.*

$$k_2 = k_p + 2k_m + 2k_o + k_x$$

where k_p, k_m, k_o, and k_x are the individual rate constants of addition to the respective positions. We hope to develop a technique for determining the various individual rate constants, but at present we can only discuss the changes observed in k_2.

Experimental

The substituted benzenes investigated were: toluene, the xylenes, mesitylene, ethylbenzene, cumene, *t*-butylbenzene, *p*-di-*t*-butylbenzene, fluoro-, chloro-, bromo-, and iodobenzenes, benzonitrile, ethyl benzoate, acetophenone, benzotrifluoride, nitrobenzene, phenol, aniline and anisole. All these compounds, acquired commercially, were purified by conventional techniques before being used.

---

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

(2) A. P. Stefani and M. Szwarc, *ibid.*, **84**, 3661 (1962).