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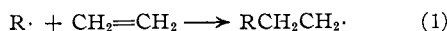
Reactivities of Aromatic Hydrocarbons toward Methyl Radicals

BY M. LEVY AND M. SZWARC

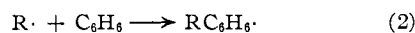
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An experimental method has been developed for determining the relative rates of addition of methyl radicals to aromatic compounds. The relative rates of addition which are denoted here as methyl affinities, were determined for the following compounds: benzene, diphenyl, naphthalene, phenanthrene, chrysene, pyrene, stilbene, benzanthracene, anthracene, naphthacene, pyridine, quinoline, isoquinoline, acridine, diphenyl ether and benzophenone. It has been found that a linear relation holds between log of methyl affinities and log of the relative rates of addition of CCl_3 radicals to a series of aromatic hydrocarbons. It is proposed to consider the slope of the resulting straight line as a measure of the intrinsic reactivities of methyl and trichloro methyl radical. Furthermore, it has been observed that there is a linear relation between log of methyl affinities and the triplet-singlet energy transitions of the aromatic compounds. This relation is discussed in terms of Polanyi's model for a chemical reaction.

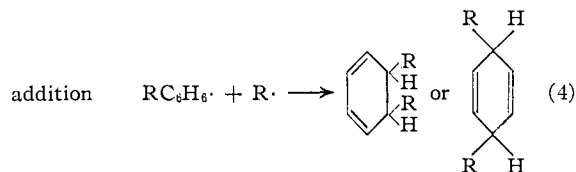
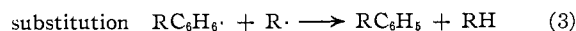
It is well known that radicals or free atoms may add to olefinic compounds producing new radicals. Such a reaction, exemplified by equation



is encountered in many processes, the polymerization of vinyl monomers being the most striking example. A considerable volume of evidence,¹⁻⁵ accumulated during the last few years, indicates that reactions similar to (1) take place when radicals interact with aromatic compounds, *e.g.*



Radicals such as $\text{RC}_6\text{H}_6\cdot$ are probably the intermediates in substitution or addition reactions, *e.g.*



We have shown recently⁶ that reaction (2) does occur when methyl radicals interact with benzene. Further investigation has resulted in the development of a method which permits a quantitative determination of the relative abilities of aromatic compounds to add methyl radicals. In this communication, we report the values for the relative rates of addition of methyl radicals to a number of aromatic compounds, and discuss their significance in relation to other radical reactions.

Description of the Method.—Kharasch and his co-workers⁷ have shown that the thermal decomposition of acetyl peroxide generates methyl radicals.⁸

(1) M. Magat and R. Boneme, *Compt. rend.*, **232**, 1657 (1951); *Faraday Soc. Disc.*, **10**, 226 (1951).

(2) W. H. Stockmayer and L. H. Peebles, *THIS JOURNAL*, **75**, 2278 (1953).

(3) C. S. Marvel and W. S. Anderson, *ibid.*, **75**, 4600 (1953).

(4) E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953).

(5) (a) I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 2695 (1952); (b) J. R. Dunn and W. A. Waters, *ibid.*, 580 (1954).

(6) M. Levy, M. Steinberg and M. Szwarc, *THIS JOURNAL*, **76**, 3439 (1954).

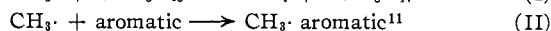
(7) M. S. Kharasch and M. T. Gladstone, *ibid.*, **65**, 15 (1943); M. S. Kharasch, E. J. Jensen and W. H. Urry, *J. Org. Chem.*, **10**, 386 (1945).

(8) It is still an unsettled problem whether reactions which involve methyl radicals are caused by "free" methyl radicals or by acetate radicals which decarboxylate in the course of the reaction. In our problem, however, the distinction between these two alternatives is relatively unimportant.

It was shown elsewhere^{6,9} that this decomposition if carried out in a *highly diluted* solution of the peroxide in isoöctane, yields carbon dioxide, methane and ethane in quantities which obey the stoichiometric relation

$$(\text{CH}_4 + 2\text{C}_2\text{H}_6)/\text{CO}_2 = 1$$

The addition of an aromatic compound to such a solution decreases the amount of methane formed, without affecting, however, the yields of carbon dioxide or of ethane produced by the decomposition.¹⁰ It seems, therefore, that the following two reactions compete for methyl radicals



and that reaction II is responsible for the decrease in the fraction of methyl radicals converted to methane in the presence of an aromatic compound.

Denoting by k_I and k_{II} the bimolecular rate constants of reactions I and II, we conclude that

$$k_{II}/k_I = \left\{ \frac{\text{(the decrease in CH}_4 \text{ formed)}}{\text{(the amount of CH}_4 \text{ formed)}} \right\} \cdot \frac{X_{\text{C}_8\text{H}_{18}}}{X_{\text{aromatic}}}$$

In this equation the "amount of CH_4 formed" denotes the amount of methane actually produced in the reaction; the "decrease in CH_4 formed" is given as the difference between the amounts of methane formed in the absence of an aromatic compound and in its presence; and $X_{\text{C}_8\text{H}_{18}}$ and X_{aromatic} represent the molar fractions of isoöctane and of the aromatic compound present in the reacting mixture.

Since the decomposition of each mole of acetyl peroxide produces 2 moles of carbon dioxide and 2 moles of methyl radicals (the latter appearing eventually as methane, ethane or the addition complex), it is convenient to express the ratio

(the decrease in CH_4 formed)/(the amount of CH_4 formed) in the form

$$\frac{\{(\text{CH}_4/\text{CO}_2)_{\text{solvent}} - (\text{CH}_4/\text{CO}_2)_{\text{ar}}\}}{(\text{CH}_4/\text{CO}_2)_{\text{solvent}}}$$

is a constant term, giving the ratio

(9) M. Levy and M. Szwarc, *THIS JOURNAL*, **76**, 5981 (1954).

(10) It has been shown elsewhere (ref. 9) that in a diluted solution of acetyl peroxide the formation of ethane has to be attributed to a cage reaction. Hence, the number of "free" methyl radicals (or acetate radicals) which are available for reactions is given at $2 \cdot (1 - g) \times$ [number of molecules of acetyl peroxide decomposed], where g denotes the probability for a cage formation of ethane. Of course, g is independent of the concentration of the peroxide, and it is unaffected by the presence of an aromatic compound in the solution.

(11) The symbol " $\text{CH}_3\cdot \text{aromatic}$ " denotes the initial intermediate addition product.

of these two products formed in pure isoöctane, while $(\text{CH}_4/\text{CO}_2)_{\text{ar}}$ denotes the ratio of these two products formed in a solution containing an aromatic compound.

The equation derived for $k_{\text{II}}/k_{\text{I}}$ is valid only if the molar fractions of isoöctane and of the aromatic compounds in solution remain constant throughout the experiment. This is substantially correct if the fraction of aromatic compound consumed in the reaction is small (say a few per cent. only). In the more general case, the decrease in the amount of CH_4 formed is given by the integral

$$\int_0^t k_{\text{II}} C [\text{CH}_3] dt$$

where C denotes the variable concentration of the aromatic compound. Solving the appropriate differential equations, without any approximation, leads to the following equation for $k_{\text{II}}/k_{\text{I}}$

$$k_{\text{II}}/k_{\text{I}} = \frac{(\text{CH}_4/\text{CO}_2)_{\text{solvent}} - (\text{CH}_4/\text{CO}_2)_{\text{ar}}}{(\text{CH}_4/\text{CO}_2)_{\text{ar}}} \times \{ X_{\text{C}_6\text{H}_6}/X_{\text{aromatic}} \}$$

where f , the correction term, is given by the expression

$$f = \frac{1}{d} \times \ln(1 - d)$$

d denoting the fraction of the aromatic compound which reacted during the experiment.

In our experiments, the concentration of the peroxide was of the order 10^{-2} mmoles/cc. If the molar fraction of the aromatic compound is 0.01, *i.e.*, 1%, then its amount is of the order 10^{-1} mmoles/cc. Hence, the above correction is significant only for experiments in which $X_{\text{aromatic}} < 0.01$, and the fraction of decomposition of the peroxide is very high.

Results

The experimental technique has been described in a previous communication⁹ to which the reader is referred. The aromatic compounds used in this investigation were obtained commercially and purified, if necessary, by standard techniques. Melting points were taken as the criteria of the purity of the compounds used. The experiments were carried out with 10-cc. portions of approximately 10^{-2} M peroxide solution in isoöctane which contained the appropriate amount of an aromatic compound. The deaerated mixtures were immersed in a constant temperature bath, heated for 2 hours and then analyzed for methane, carbon dioxide and ethane. The experimental data are listed in Table I. The ratio CH_4/CO_2 for the peroxide solution in isoöctane (in the absence of aromatics) was determined in several experiments, and the average values (0.805 at 65°, and 0.802 at 85°) were used for the computations of $k_{\text{II}}/k_{\text{I}}$ values listed in the fourth column of Table I. The last column in Table I gives the unimolecular rate constants for the decomposition of acetyl peroxide measured by the amount of CO_2 produced. The percentage decomposition of the peroxide was about 5% in experiments carried out at 65°, and 50 to 60% in experiments performed at 85°.

Some aromatic compounds, such as chrysene or naphthalene, have little solubility in isoöctane and

in order to overcome this difficulty toluene was used as an alternative solvent. The use of another solvent naturally changes the rate constant k_{I} , so that the new results are expressed in terms of $k_{\text{II}}/k_{\text{I}}$, k_{I} being generally different from k_{I} .

TABLE I

T , °C.	Mole % of aromatic in the soln.	CH_4/CO_2	$k_{\text{II}}/k_{\text{I}}$	k_{II} $\times 10^5$, sec. ⁻¹
65	25% Benzene	0.740	0.26	0.88
65	50% Benzene	.605	.33	.95
65	75% Benzene	.433	.29	.955
85	25% Benzene	.697	.45	13.4
85	50% Benzene	.582	.38	14.0
85	75% Benzene	.402	.33	14.3
65	5% Biphenyl	0.750	1.4	0.80
65	10% Biphenyl	.682	1.6	0.81
85	5% Biphenyl	.725	2.0	11.2
85	10% Biphenyl	.665	1.9	11.1
85	20% Biphenyl	.550	1.8	10.6
65	5% Naphthalene	0.545	9.1	0.85
65	10% Naphthalene	.417	8.4	.86
65	20% Naphthalene	.253	8.7	.91
65	20% Naphthalene	.253	8.7	.89
85	5% Naphthalene	.536	9.4	12.7
85	10% Naphthalene	.412	8.5	11.8
85	20% Naphthalene	.267	8.0	11.3
65	5% Phenanthrene ^a	0.527	10.0	0.82
65	10% Phenanthrene ^a	.358	11.3	0.87
85	5% Phenanthrene ^a	.518	10.4	12.2
85	10% Phenanthrene ^a	.343	12.0	12.8
85	20% Phenanthrene ^a	.221	10.5	12.2
85	0.25% Pyrene	0.727	41	9.8
85	0.75% Pyrene	.575	52	10.6
85	1.00% Pyrene	.521	53	10.6
65	0.5% Stilbene	0.513	113	0.93
65	1.0% Stilbene	.392	104.5	0.93
85	0.5% Stilbene	.572	80	12.3
85	1.0% Stilbene	.488	64	10.4
85	1.0% Stilbene	.432	84.5	12.6
85	2.0% Stilbene	.318	74.5	11.8
85	2.5% Stilbene	.309	62	9.9
65	0.5% Anthracene	0.275	385	0.98
85	.125% Anthracene	.525	420	13.6
85	.25% Anthracene	.442	326	12.6
85	.50% Anthracene	.313	310	12.6
85	.50% Anthracene	.336	276	11.2
65	20% Pyridine	0.615	1.2	1.23
65	30% Pyridine	.482	1.5	1.48
85	10% Pyridine	.730	0.9	12.9
85	20% Pyridine	.615	1.2	13.4
85	30% Pyridine	.485	1.5	12.4
65	10% Quinoline	0.327	13.2	1.04
65	20% Quinoline	.195	12.5	1.30
65	30% Quinoline	.111	14.4	1.46
85	10% Quinoline	.357	11.2	12.7
85	20% Quinoline	.211	11.2	12.4
85	30% Quinoline	.135	11.5	12.3
85	10% Isoquinoline	0.308	14.4	8.6
85	20% Isoquinoline	.178	14.0	9.5
85	30% Isoquinoline	.115	14.0	7.8
85	1% Acridine	0.290	174	7.9
85	2% Acridine	.185	164	7.9
65	5% Benzophenone	0.660	4.2	0.83
85	5% Benzophenone	.638	4.9	11.4
85	10% Benzophenone	.550	4.1	11.2
85	20% Benzophenone	.395	4.1	11.6

TABLE I (Continued)

T , °C.	Mole % of aromatic in the soln.	CH_4/CO_2	k_{II}/k_I	k_u $\times 10^5$, sec. ⁻¹
85	10% Diphenyl ether	0.725	0.95	9.9
85	20% Diphenyl ether	.640	1.0	9.0
85	30% Diphenyl ether	.585	0.9	8.8

^a The phenanthrene used in these experiments was freed from anthracene by treating it with maleic anhydride. The values reported in our preliminary note (*J. Chem. Phys.*, **22**, 1621 (1954)), refer to the compound purified by crystallization only, which contained apparently some anthracene impurities.

The data obtained with toluene as a solvent are listed in Table II. Computations are based on a CH_4/CO_2 ratio of 0.665 obtained for toluene (in the absence of an aromatic compound) at 85°. The k_{II}/k_I' values were correlated with k_{II}/k_I values, measured in iso-octane solution, by carrying out a series of experiments with the same aromatic compounds in both solvents. The results given in Table III show that k_{II}/k_I' values are lower by a factor of 3 than the respective k_{II}/k_I values.

TABLE II
Toluene used as a solvent; $T = 85^\circ$

Mole % of cpd.	CH_4/CO_2	k_{II}/k_I'	k_{II}/k_I recalcd.	k_u $\times 10^5$, sec. ⁻¹
10% Naphthalene	0.477	3.5		10.5
0.5% Anthracene	.447	97.5		9.7
1.0% Anthracene	.377	114		12.4
10% Quinoline	.478	3.5		10.4
1.0% Pyrene	.557	19.2		12.4
0.5% Chrysene	0.645	7.4	23.0	14.2
1.0% Chrysene	.616	7.9		12.0
0.5% Benzantracene	0.506	62.5	187	12.1
1.0% Benzantracene	.420	58.5		12.5
1.0% Benzantracene	.410	62.5		13.4
2.0% Benzantracene	.286	66.5		12.7
0.98% Triphenylene	0.603	11.2	34	14.7
0.03% Naphthacene ^a	0.592 ^a	765 ^a	3700	1.1 ^a
0.03% Naphthacene ^a	.576 ^a	880 ^a		1.1 ^a

^a These experiments were performed in *p*-xylene solution at 65°.

TABLE III
COMPARISON OF k_{II}/k_I' 'S IN DIFFERENT SOLVENTS
All these data refer to 85°

Aromatic	k_{II}/k_I in iso-octane	k_{II}/k_I' in toluene	$(k_{II}/k_I)/$ $(k_{II}/k_I') =$
Naphthalene	8.52	3.55	2.4
Quinoline	11.2	3.52	3.2
Phenanthrene	17.3	5.2	3.3
Pyrene	52.8	19.2	2.75
Anthracene	330	97.5	3.4
Quinone	6000	2000	3.0

Discussion

The following conclusions emerge clearly from inspection of the data collected in Tables I, II and III.

1. The rate of the unimolecular decomposition of acetyl peroxide is essentially unaffected by the presence of varying amounts of different aromatic compounds. Its value is about $0.8-0.9 \times 10^{-5}$ sec.⁻¹ at 65° and $11-12 \times 10^{-5}$ sec.⁻¹ at 85°. The addition of bases like pyridine definitely accelerates the decomposition rate. This effect seems to be

quite general, and has been observed in the decomposition of other peroxides.¹²

2. Although the molar fractions of the aromatic compounds were varied by factors as high as 4, the ratio k_{II}/k_I remains essentially constant for a given compound. This is strong evidence justifying our interpretation of its significance.

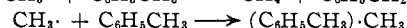
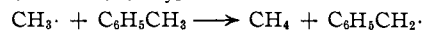
3. Since activation energies for reactions I (abstraction of hydrogen atom from the solvent) and II (addition to the aromatic compound) are both low, not exceeding probably 10 kcal./mole, one would expect little change, if any, in k_{II}/k_I determined at 65 and 85°, respectively. This is in a substantial accord with the data presented in Tables I and II.

On the other hand, the activation energy of the decomposition of acetyl peroxide is high (about 30 kcal./mole), and thus the rate of the decomposition increases over tenfold as the temperature is raised from 65 to 85°. Hence, the stationary concentration of methyl radicals is about 10 times higher at 85° than it is at 65°, and consequently the constancy of k_{II}/k_I shows that this entity is essentially independent of the stationary concentration of methyl radicals, confirming again our basic assumption.

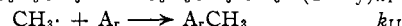
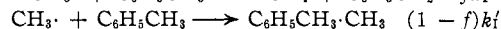
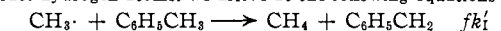
4. Further evidence in favor of our kinetic scheme is provided by the comparison of k_{II}/k_I obtained in iso-octane solution with k_{II}/k_I' obtained in toluene solution. It follows from our assumptions that the ratio $(k_{II}/k_I)/(k_{II}/k_I')$ obtained for the same aromatic compound should be a constant, namely, k_I'/k_I . Such a comparison is shown in Table III. In spite of the great variation in the individual values of k_{II}/k_I the ratio of k_I'/k_I remains constant. This result means that methyl radicals abstract hydrogen atoms from toluene about three times more readily than from iso-octane.¹³

(12) P. D. Bartlett and K. Nozaki, *THIS JOURNAL*, **69**, 2299 (1947).

(13) The last statement needs some clarification. Methyl radicals react with toluene in two ways



Indeed, the ratio $(\text{CH}_4 + 2\text{C}_6\text{H}_5\text{CH}_2)/\text{CO}_2$ obtained in experiments carried out in pure toluene is less than 1, indicating clearly that some addition reaction takes place in the solvent.⁹ If we denote by k_I the bimolecular rate constant for the reaction $\text{CH}_3\cdot + \text{C}_6\text{H}_5\text{CH}_3$ regardless what the products are, and by f the fraction of methyl radicals which abstract hydrogen atoms, we arrive at the following equations



The ratio $(\text{CH}_4/\text{CO}_2)_T$ in experiments carried out in the absence of an aromatic compound is $f(1-g)$, where g denotes the fraction of methyl radicals which produce ethane by the cage reaction (g is independent of the concentration of acetyl peroxide and of the concentration of the aromatic compound, see ref. 9). In the presence of an aromatic compound the fraction of methyl radicals which abstract hydrogen atoms is given by

$$(\text{CH}_4/\text{CO}_2)_{A_r} = (1-g)k_I'fX_T/(k_I'X_T + k_{II}X_{A_r})$$

hence

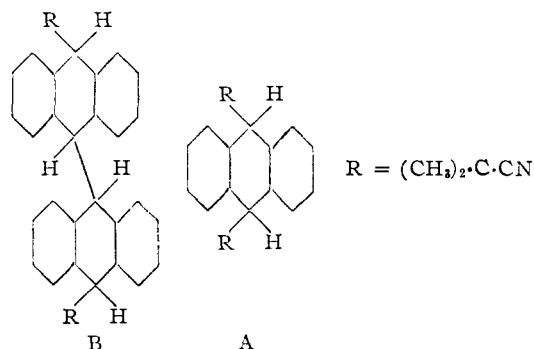
$$(\text{CH}_4/\text{CO}_2)_T - (\text{CH}_4/\text{CO}_2)_{A_r} = (1-g)f k_{II}X_{A_r}/(k_I'X_T + k_{II}X_{A_r})$$

and finally

$$k_{II}/k_I' = \frac{(\text{CH}_4/\text{CO}_2)_T - (\text{CH}_4/\text{CO}_2)_{A_r}}{(\text{CH}_4/\text{CO}_2)_{A_r}} \times \frac{X_T}{X_{A_r}}$$

The final result is the same as that deduced previously for the case of iso-octane; the only difference lies in the meaning of k_I' which denotes now the rate constant of the reaction of toluene with methyl radicals regardless of the nature of the products.

The above survey of experimental results shows that the proposed mechanism is well substantiated. Nevertheless, it is desirable to discuss critically the underlying assumptions. There is little doubt that radicals may add to aromatic compounds. The most direct evidence is brought up by the work of Kooyman and Bickel¹⁴ who isolated the products by addition of $(\text{CH}_3)_2\text{C}\cdot\text{CN}$ radicals to anthracene. Both compounds (A) and (B) were identified as products of the reaction.



While (A) results from the reaction of the initial complex $\text{Ar}\cdot\text{R}$ with another R radical, (B) represents the product of dimerization of two initial complexes $\text{Ar}\cdot\text{R}$.

The next point which needs consideration is the fate of the initial complex $\text{Ar}\cdot\text{CH}_3$. Our mechanism assumes implicitly that $\text{Ar}\cdot\text{CH}_3$ does not react further with methyl radicals. Such an assumption seems to be justified under our experimental conditions, as is shown clearly by the fact that *all* methyl radicals, produced in a dilute solution of acetyl peroxide in isoöctane, are accounted for in the form of methane or ethane; *i.e.*, the ratio $(\text{CH}_4 + 2\text{C}_2\text{H}_6)/\text{CO}_2$ obtained from 10 experiments is 0.98 ± 0.013 . This means that the probability for a methyl radical to recombine with a solvent radical is much lower than the probability of its reaction with a solvent molecule. Consequently, the stationary concentration of solvent radicals is much higher than that of methyl radicals, and the former radicals disappear eventually by reacting in pairs. The same argument applies to the situation existing in the presence of an aromatic compound, and we conclude that the initial complexes $\text{Ar}\cdot\text{CH}_3$ disappear either by reactions involving solvent radicals R, or by reaction involving two $\text{Ar}\cdot\text{CH}_3$ radicals. Such reactions may be dimerization or disproportionation processes.

Finally, let us consider the reaction of abstraction of a hydrogen atom from an aromatic molecule by a methyl radical. Such a reaction is quite conceivable, and it would be an additional source for methane formation. However, its rate constant is probably much lower than that for the reaction with iso-octane¹⁵ and therefore its importance would be negligible for all the cases in which isoöctane is in a great excess. The only case in which the concentration of an aromatic compound is high is that of benzene, and we feel that even

(14) A. F. Bickel and E. C. Kooyman, *Rec. trav. chim.*, **71**, 1137 (1952).

(15) We deal with aromatic compounds which do not possess side chains, *i.e.*, no labile hydrogen atoms.

for this compound our determination of k_{11}/k_1 is not greatly in error.

Scale of Methyl Affinities.—We are now in a position to introduce the scale of relative reactivities of aromatic compounds toward methyl radicals.¹⁶ We propose to take the relative values of the rate constants k_{11} as a measure of this property of an aromatic compound, and we attribute arbitrarily the value of unity to the relative reactivity of benzene. Taking the average value of k_{11}/k_1 obtained at 85° ¹⁷ for each of the investigated compounds and dividing it by the k_{11}/k_1 value obtained for benzene, we build up the scale of relative methyl affinities of aromatic compounds which is presented in Table IV.

TABLE IV
THE RELATIVE REACTIVITIES: BENZENE TAKEN AS UNITY

Compound	Relative methyl affinities	Compound	Relative methyl affinities
Benzene	1	Anthracene	820
Diphenyl	5	Naphthacene	9250
Naphthalene	22	Pyridine	3
Phenanthrene	27	Quinoline	29
Chrysene	57.5	Isoquinoline	36
Pyrene	125	Acridine	430
Stilbene	183	Benzophenone	11
Benzoanthracene	468	Diphenyl ether	2.5

Inspection of Table IV shows clearly that the reactivities of aromatic compounds increase rapidly with the increasing conjugation in the molecules. This is shown clearly by comparing the methyl affinities of benzene, diphenyl and diphenyl ether. The latter molecule is built up from 2 non-conjugated benzene rings and we would expect, therefore, a value of 2 for its methyl affinity. Hence, it was gratifying to find a value 2.5 for the methyl affinity of diphenyl ether. On the other hand, the two phenyls are conjugated in the molecule of diphenyl and its methyl affinity is considerably greater, namely, 5. The case of benzophenone is of some interest. Its methyl affinity is 11, and it might result from the presence of the $\text{C}=\text{O}$ bond conjugated with phenyl groups. This result poses the question whether methyl radicals attack initially the aromatic rings or the $\text{C}=\text{O}$ bonds.¹⁸ At present there is not enough information to solve this problem, but we hope to study it more fully in future investigations.

The reactivities of heterocyclic compounds are closely related to the reactivities of the corresponding isocyclic compounds. On the whole, the presence of a nitrogen atom in the ring seems to activate the molecule, the effect however decreases with the increasing size of the molecule. The position of the pair acridine-anthracene seems to be anomalous in this respect. No explanation for this anomaly is offered at this stage of the investigation.

(16) We shall refer to this entity as methyl affinity for the sake of compactness of the language.

(17) The temperature of 85° has been chosen arbitrarily. At this temperature, the experimental values are more reproducible and accurate than at 65° .

(18) Since the $\text{Ar}\cdot\text{CH}_3$ complex formed initially might isomerize in course of a reaction leading to the final product, the isolation of the final product is not sufficient for answering the problem.

The Comparison of Reactivities of Various Radicals.—Several groups of workers investigated recently the reactivities of various radicals toward aromatic hydrocarbons. Most of these studies led to qualitative information only. Thus, *e.g.*, Magat and Boneme¹ found that radicals formed in the thermal polymerization of styrene show a decreasing reactivity toward the following compounds: benzopyrene > 20-methylcholanthrene > phenanthrene > 2-methylanthracene > dibenzanthracene, while their reactivities toward pyrene and chrysene seem to be negligibly small. Roitt and Waters⁵ reported a slightly different order of reactivities of aromatics toward radicals generated by the decomposition of benzoyl peroxide. The order of reactivities was: benzopyrene >> anthracene, benzanthracene > dibenzanthracene >> phenanthrene, chrysene.

Quantitative information on this subject was provided by the studies of Kooyman and Farenhorst and of Dunn and Waters. Kooyman and Farenhorst⁴ studied the addition of CCl_3 radicals to *n*-hexadecene and to styrene. They found that the reaction is retarded by various aromatic hydrocarbons and from the extent of retardation they were able to measure the relative rates of addition of CCl_3 radicals to aromatic compounds. The comparison of their data with those reported in the present paper is very instructive. Figure 1 shows a plot of logarithms of the relative addition constants of CCl_3 radicals *versus* those of methyl radicals, which results in a straight line. The point representing naphthacene seems to be displaced. We believe that reactivity of naphthacene has been incorrectly determined by Kooyman, the error probably resulting from the exceedingly low solubility of naphthacene. The reactivity of benzene toward CCl_3 radicals is so low that Kooyman could estimate only its upper limit, namely, $k_r < 10^{-3}$. From our linear relation we would predict the reactivity of benzene $k_r = 10^{-4}$.

It is interesting to notice that for the series of investigated hydrocarbons the k_r values vary within six powers of ten while the reactivities toward methyl radicals vary within four powers of ten only. We consider this fact as important, and we believe that it reflects the difference in intrinsic reactivities of CCl_3 and CH_3 radicals. An extremely reactive radical will react approximately at the same rate with substrates of various reactivities; on the other hand, the rate of attack of a radical of a low reactivity will vary considerably for different substrates. We propose, therefore, to consider the slope of the straight line shown in Fig. 1, estimated by the least square method at 1.95, as a measure of the ratio of the intrinsic reactivities of methyl and trichloromethyl radicals, and we hope to develop this subject further in a forthcoming publication.

The inhibition of benzaldehyde autooxidation by aromatic compounds was studied by Dunn and Waters.^{5b} These workers deduce, from their kinetic studies, the relative rate constants of addition of PhCOO_2 radical to aromatic hydrocarbons. In view of the complicated nature of the reaction, and of uncertainties in assumptions introduced, the

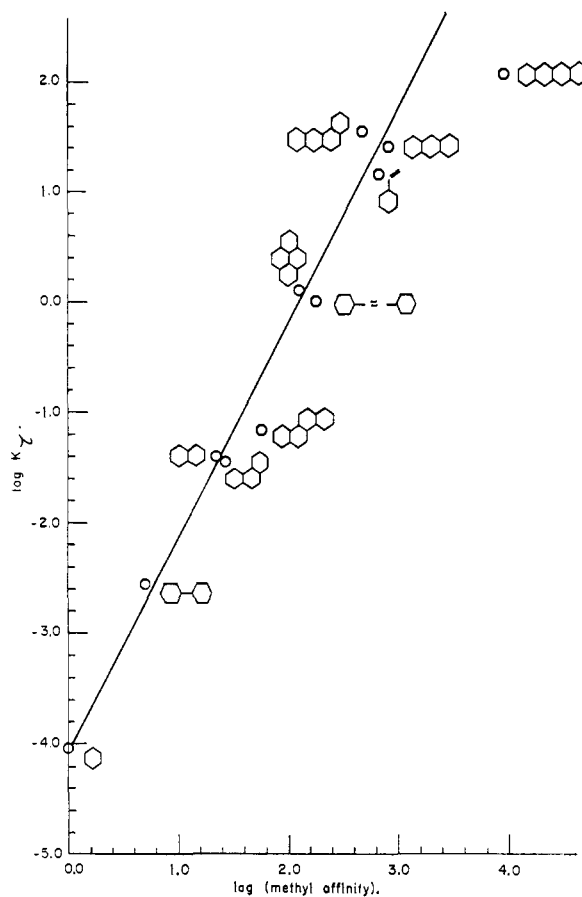


Fig. 1.

values of Dunn and Waters should be considered as less reliable than those of Kooyman and Farenhorst. Nevertheless, the plot of their rate constants *versus* those of methyl radicals (on a log-log scale) results also in a straight line, and from the slope of this line we conclude that the intrinsic reactivity of the PhCOO_2 is about the same as the intrinsic reactivity of CCl_3 radical.¹⁹

The Mechanism of the Addition Process.—It was pointed out by Kooyman and Farenhorst⁴ that an approximate linear relation exists between the logarithms of the addition constants and the maximum free valencies calculated for the respective aromatic compounds.²⁰ Of course, the same type of relation must hold for the relative methyl affinities, since there is a linear relation between the logarithms of the latter and $\log k_r$. The existence of such a relation implies that the radical adds to a particular carbon atom, namely, to the one endowed with a maximum free valency.

One can look upon the problem of addition of a radical to an aromatic hydrocarbon from a different viewpoint. The ground state of an aromatic hydrocarbon is a singlet. It is plausible to expect, however, that in the transition state it acquires the electronic configuration of a triplet (the uncoupling of one pair of electrons would be necessary to pro-

(19) Unfortunately, this conclusion is based on results obtained for three compounds only, chrysene, benzanthracene and anthracene.

(20) For the sake of this correlation the addition constants are divided by the number of carbon atoms corresponding to the maximum free valency.

vide an electron for the formation of a new bond).

It has been suggested by one of us²¹ that the course of the addition reaction may be represented by the heavy line shown in the energy diagram, Fig. 2. The energy of the system radical-aromatic

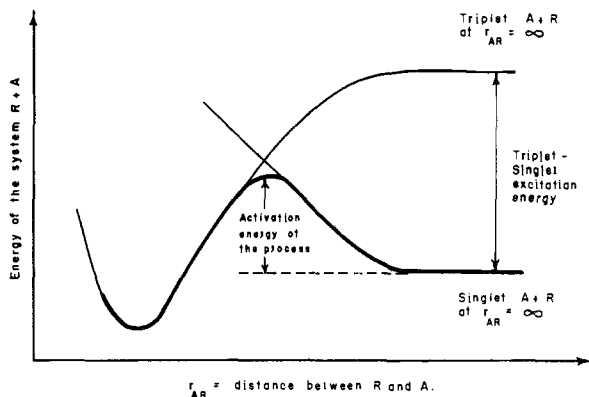


Fig. 2.

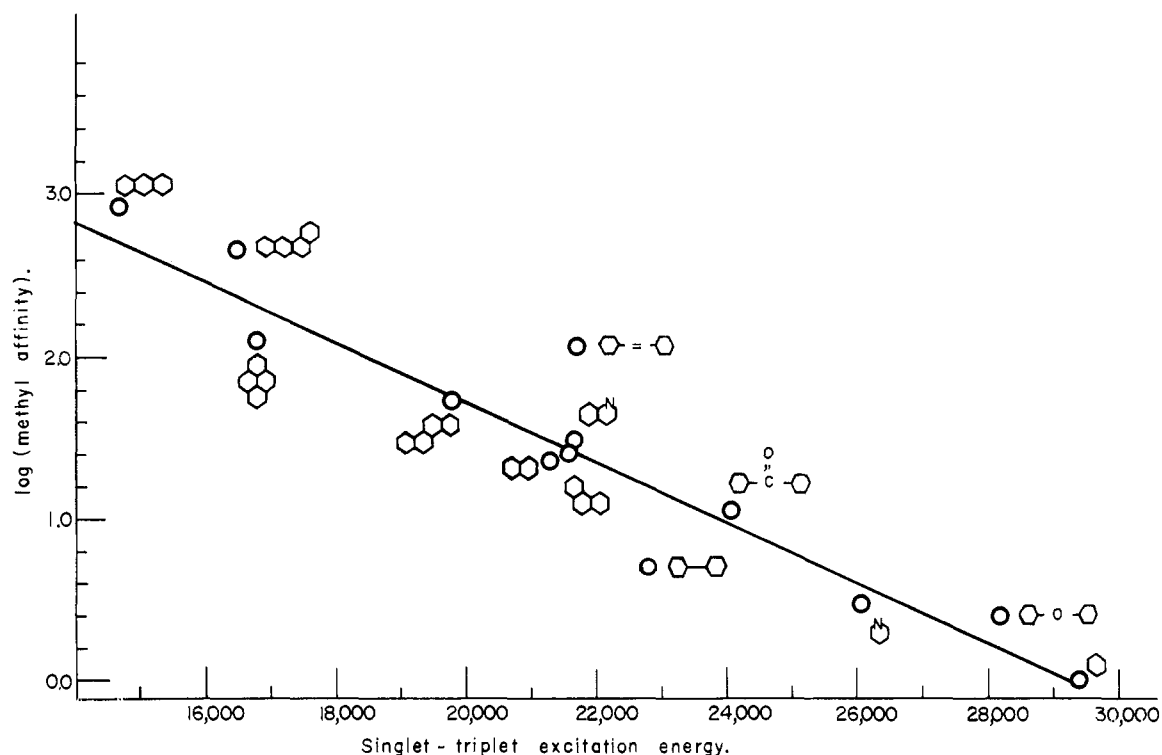


Fig. 3.

molecule in its ground state (singlet state) is given by the rising curve (for the decreasing r_{AR}). The increase in energy is due to the repulsive force resulting from the interaction between a radical and an aromatic molecule in its singlet state. On the other hand, the interaction between an excited triplet molecule and a radical results in an attractive force leading to the formation of a chemical bond. Consequently, the energy of a system radical-triplet state aromatic molecule decreases with decreasing distance between the components, and the curve has the shape of the familiar Morse curve. The actual path of the process results from the

(21) M. Szwarc and L. A. Essede, *J. Chem. Phys.*, in press.

crossing from the first repulsion curve to the second attraction curve, the hump corresponding to the transition state.

If one deals with a series of reactions of the above type in which the same radical R interacts with various aromatic molecules A_1, A_2, \dots one deduces, applying the well known approach of Polanyi,²² that the differences in the activation energies ΔE_a are proportional to the differences in the respective singlet-triplet excitation energies ΔE_{S-P} , *i.e.*

$$\Delta E_a = \alpha \Delta E_{S-P}$$

This relation is approximate. In its derivation it is assumed that the slopes of the crossing lines remain constant for the series of reactions, and it does not account for the rounding at the intersection point which is caused by resonance between the two levels.

Assuming now that the differences in the respective activation energies are responsible for the variations in the rate constants of the addition reaction, one concludes that a linear relation should exist

between log of these rate constants and the respective singlet-triplet excitation energy. Such a relation, for the reaction involving methyl radicals, is shown in Fig. 3, the relevant data being given in Table V.

It is striking to notice that the points represented in Fig. 3 refer to molecules belonging to various classes of compounds, such as hydrocarbons, heterocyclic nitrogen bases, ketones and ethers. There are only two points which seem to be displaced; the one corresponds to diphenyl and the other to stilbene. However, the reactivity of the latter re-

(22) R. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 604 (1935); M. G. Evans and M. Polanyi, *ibid.*, **34**, 11 (1938).

