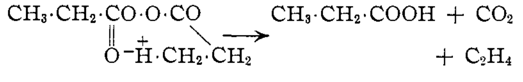
as one proceeding by a proton transfer rather than by a hydrogen atom transfer, namely



$$\begin{matrix} CH_3\cdot CH_2\cdot CO\cdot O\cdot CO & & CH_3\cdot CH_2\cdot COOH + CO_2 \\ \| \quad + \quad \diagdown & \longrightarrow & \\ O^{-}H\cdot CH_2\cdot CH_2 & & + C_2H_4 \end{matrix}$$

This proposition was considered and was shown to be unacceptable, since it would require an increase in the amount of ethylene present amongst the products of decomposition proceeding in polar solvents. The analysis of C_2 hydrocarbons formed in these solvents demonstrated that the amount of ethylene formed is approximately the same as that formed in isoöctane solution. Furthermore, since ethylene formed by reaction (6) does not result from free radicals, the residual C_2 hydrocarbons formed in polar solvents and in the presence of quinone should be produced in greater quantity than the residual C_2 hydrocarbons formed under analogous conditions in isoöctane solution. Experiments have shown that this is not the case. This point is well demonstrated by the results obtained in nitrobenzene solution. Nitrobenzene is an efficient scavenger for radicals, and thus in nitrobenzene solution only the "residual" C_2 hydrocarbons (*i.e.*, those which are not produced from free, floating ethyl radicals) should be the products of the reaction. One finds in Table IV that the C_2H_6/CO_2 in nitrobenzene is about 0.09, while the C_2H_6/CO_2 formed in isoöctane and in the presence of an excess of quinone is about 0.08.[20] The agreement is good.

In conclusion, we wish to acknowledge the generous support of this investigation by The National Science Foundation.

[20] C_2H_6/CO_2 means C_2 hydrocarbons/CO_2.

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

Ethyl Affinities of Aromatic and Olefinic Compounds

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The relative rates of addition of ethyl radicals to aromatic compounds have been determined. The respective relative rate constants, referred to as ethyl affinities, parallel the corresponding methyl affinities. The plot of the log of ethyl affinities *versus* log of methyl affinities gives a straight line with a slope of unity, *i.e.*, the intrinsic reactivities of methyl and ethyl radicals seems to be identical. On the other hand, ethyl radicals appear to be less reactive toward solvent than methyl radicals. This difference in behavior toward hydrogen abstraction on one hand and the addition to aromatic compounds on the other is fully discussed.

In a series of recent papers,[1-4] it was shown that methyl radicals may add to aromatic or olefinic compounds, such additions being represented by equation 1

$$CH_3 + A \longrightarrow A\cdot CH_3 \qquad (1)$$

In this equation, A denotes a molecule of an aromatic or an olefinic compound, while $A\cdot CH_3$ represents the primary product of the reaction. $A\cdot CH_3$ is itself a radical and, therefore, it cannot be the final and ultimate product which could be isolated from the reacting mixture. In spite of this the rate constants of reaction (1) can be measured, and recently a simple method has been developed[1-4] for determining the relative values of these rate constants. This is achieved by generating methyl radicals in an aliphatic hydrocarbon solvent, HS, which contains the required amount of an aromatic compound, A. Under suitable experimental conditions HS and A compete for methyl radicals, the reaction with the solvent proceeding according to equation 2

$$CH_3 + HS \longrightarrow CH_4 + S \qquad (2)$$

while the aromatic compound A reacts according to equation 1. The ratio of the rate constants k_1/k_2 then can be evaluated if the amounts of methane and $A\cdot CH_3$ formed in the process are determined.

Determination of the ratios k_1/k_2 for a series of different compounds, A, dissolved in the same solvent HS yields, therefore, the relative rate constants of addition of methyl radicals to various molecules of type A, and such values have been termed the methyl affinities of molecules A. For the sake of convenience, the methyl affinity of benzene has been chosen as unity; such a convention, however, does not affect at all the generality of the concept of methyl affinities.

The present investigation has been conducted with the intention of expanding the previous studies to reactions involving ethyl radicals. By analogy to the term "methyl affinities," we will refer to the relative rates of addition of ethyl radicals to various aromatic and olefinic compounds as "ethyl affinities." The method used in determining these entities is outlined below.

Determination of Ethyl Affinities.—An investigation of the pyrolysis of gaseous propionyl peroxide[5] and a study of its decomposition in a variety of solvents[6] show that this compound decomposes in a unimolecular fashion according to equation 3

$$(C_2H_5\cdot COO)_2 \longrightarrow 2C_2H_5\cdot CO_2 \qquad (3)$$

and the latter reaction is followed by a rapid decarboxylation of the propionate radical.[7]

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(1) M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

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

(3) A. Rembaum and M. Szwarc, *ibid.*, **77**, 4468 (1955).

(4) F. Leavitt, M. Levy, M. Szwarc and V. Stannett, *ibid.*, **77**, 5493 (1955).

(5) A. Rembaum and M. Szwarc, *J. Chem. Phys.*, **23**, 909 (1955).

(6) J. Smid, A. Rembaum and M. Szwarc, THIS JOURNAL, **78**, 3315 (1956).

(7) The problem of decarboxylation of $CH_3CO_2\cdot$, $C_2H_5CO_2\cdot$ and $C_3H_7CO_2\cdot$ radicals is discussed at length in a paper by Jaffe, Prosen and Szwarc, in course of publication. These workers demonstrated that decarboxylation of the above radicals is *exothermic* to an extent of 12-14 kcal./mole, in contradistinction to decarboxylation of $PhCO_2\cdot$ radicals which is *endothermic* to an extent of about 4 kcal./mole.

$$C_2H_5CO_2\cdot \longrightarrow C_2H_5 + CO_2 \qquad (4)$$

It has been shown[6] that ethyl radicals generated by reactions (3) and (4) react with aliphatic hydrocarbon solvents according to equation 5, thus yielding ethane and solvent radicals S

$$C_2H_5 + HS \longrightarrow C_2H_6 + S \qquad (5)$$

However, if an aromatic or an olefinic compound is present in the reacting mixture then, in addition to reaction (5), reaction (6) consumes a fraction of ethyl radicals

$$C_2H_5 + A \longrightarrow A\cdot C_2H_5 \qquad (6)$$

Applying now the arguments outlined in ref. 1, one deduces that

$$k_6/k_5 = \{(\text{amount of } A\cdot C_2H_5 \text{ formed})/(\text{amount of } C_2H_6 \text{ formed})\} \times X_{HS}/X_A$$

where X_{HS} and X_A denote the mole fractions of the solvent and of the aromatic compound, A, present in the reacting mixture. This formula applies in the case when the mole fractions X_{HS} and X_A remain essentially constant throughout the whole course of the reaction, and this condition was fulfilled in all experiments by a judicious choice of the concentration of the peroxide and of its extent of decomposition.

The determination of the amount of $A\cdot C_2H_5$ formed in the process is achieved by applying the method described in ref. 1. In the absence of an aromatic compound, A, all ethyl radicals available for reactions (5) or (6) react with the solvent yielding ethane. On the other hand, in an experiment conducted under identical conditions but in presence of a compound A some ethyl radicals are consumed by reaction (6) and consequently the yield of ethane is decreased. The decrease in the amount of ethane formed, referred to as "ethane loss," measures therefore the amount of $A\cdot C_2H_5$ formed in the process.

The determination of the amount of ethane formed in the reaction requires further elaboration. It was shown in the preceding paper[6] that at a constant temperature and in a given solvent a constant fraction of ethyl radicals, formed by the decomposition of the peroxide, is consumed by the liquid "cage" reaction, because a pair of radicals formed from a single molecule of the peroxide has some finite probability of mutual interaction before the partners diffuse into the surrounding medium and lose their identity. It was shown, furthermore, that such a cage reaction involves disproportionation as well as recombination of radicals. Consequently, the amount of C_2 hydrocarbon produced in the experiments with which we are concerned is composed of two quantities, the amount of ethane formed in bimolecular reaction (6) and the amount of C_2 hydrocarbons formed in the "cage" reaction. Hence, to determine the amount of ethane formed by reaction (6), one has to subtract the amount of C_2 hydrocarbons produced by the "cage" reaction from the total amount of C_2 hydrocarbons determined analytically in each experiment.

From purely experimental reasons, it is advantageous to present the results not in a form of absolute quantities of products formed but as ratios C_2H_6/CO_2, C_4H_{10}/CO_2, etc.[8] In this presentation the "ethane loss" is given by the difference

$$(C_2 \text{ hydrocarbons formed in absence of A})/CO_2 - (C_2 \text{ hydrocarbons formed in presence of A})/CO_2,$$

while the "ethane formed" is given by the difference

$$(C_2 \text{ hydrocarbons formed in presence of A})/CO_2 - (C_2 \text{ hydrocarbons formed by ``cage'' reaction})/CO_2$$

The ratio (C_2 hydrocarbons formed in absence of A)/CO_2 has been determined at 0.561 ± 0.007 by averaging the results of 14 experiments carried out in isoöctane solution at 65°. The ratio (C_2 hydrocarbons formed by "cage" reaction)/CO_2 was determined previously for the same solvent and at the same temperature to be 0.077 (see ref. 6 for details of this determination). Finally the ratios (C_2 hydrocarbons formed in presence of A)/CO_2 were determined for each individual experiment.[9] The latter values, denoted as C_2H_6/CO_2, are listed in the second column of Table I. The ratios k_6/k_5, listed in the third column of Table I, are computed then by using the formula

$$k_6/k_5 = \{(\text{ethane loss})/(\text{ethane formed})\} \times X_{HS}/X_A$$

Discussion of Results

Inspection of Table I reveals the following points. No direct reaction takes place between the peroxide and any of the compounds A added to the solution. This follows from the observation that the amount of carbon dioxide liberated in the reaction is not affected by presence of compound A, *i.e.*, the unimolecular rate constants k_u, listed in the last column of Table I and based on the amount of carbon dioxide formed, remain constant in spite of the varying amounts of compounds A added to the solution. The increase in k_u observed in the case of benzene results from the complete change of the environment. At 65° the value of k_u is about 1×10^{-5} sec.$^{-1}$ for isoöctane solution compared with about 2×10^{-5} sec.$^{-1}$ for an aromatic hydrocarbon solution.[6]

The proposed kinetic scheme seems to be justified by the constancy of k_6/k_5's which are not changed by a variation in the concentration of A even as large as sevenfold. Again, the behavior of benzene is anomalous and it will be discussed further in the latter part of this paper.

The proposed mechanism implies that *all* ethyl radicals, which escaped from the "cage," are consumed by reactions (5) or (6), and *none* reacts with the solvent radicals or the $A\cdot C_2H_5$ radicals. This assumption seems to be justified for systems involving methyl radicals, since it was shown[1] that *all* methyl radicals generated by the decomposition of acetyl peroxide in isoöctane solution are accounted for in form of methane or ethane, *i.e.*, the $(CH_4 + 2\ C_2H_6)/CO_2$ ratio was found to be unity. In the case of ethyl radicals, however, this assumption is not justified any more, since even in

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(8) See ref. 4 for further discussion of this point.

(9) The experimental details of the latter determination are described fully in the preceding paper (ref. 6). Each experiment was carried out with 10 cc. of 0.001 M solution of propionyl peroxide in isoöctane to which the required amount of the compound A was added. The deaerated solution was heated for 2 hr. at 65° and then analyzed for the products. About 7% of peroxide was decomposed in each run.

TABLE I

Mole % of A	C_2H_6/CO_2	k_6/k_5	ku × 10^6 sec.$^{-1}$
Benzene			
5	0.504	2.58	1.05
15	.427	2.25	1.08
30	.341	1.95	1.17
45	.275	1.74	1.26
60	.222	1.56	1.40
Biphenyl			
1.0	0.507	11.1	1.03
2.0	.468	11.8	1.04
4.0	.411	10.9	1.03
6.0	.368	10.4	1.06
Naphthalene			
1.0	0.316	102	0.95
3.0	.211	103	0.97
5.0	.157	96	1.00
7.0	.135	98	1.01
Phenanthrene			
0.25	0.444	128	0.95
0.50	.374	127	.95
1.0	.299	123	.96
1.5	.249	119	.97
Quinoline			
0.5	0.329	185	1.04
1.0	.248	182	1.05
1.75	.192	180	1.11
trans-Stilbene			
0.1	0.272	1490	0.96
.2	.200	1470	.98
.3	.169	1420	.95
.5	.138	1390	.93
Benzophenone			
1.0	0.401	49.7	1.04
2.0	.315	50.9	1.01
3.0	.272	48.1	1.03
Vinyl acetate			
0.1	0.475	219	0.98
.2	.420	207	.98
.3	.372	214	.98
.5	.310	216	.98

10^{-3} *M* solution of propionyl peroxide in isoöctane the ratio $(C_2H_6 + C_4H_{10})/CO_2$ is found to be on the average 0.87 at 65° (see the preceding paper). It appears, therefore, that under these conditions, about 13% of ethyl radicals formed by the decomposition react with solvent radicals. However, we can conclude *a posteriori*, in view of the constancy of k_6/k_5, that in the present experiments the fraction of ethyl radicals reacting with the solvent radicals or with $A{\cdot}C_2H_5$ radicals is essentially the same as that interacting with solvent radicals in absence of compound A. To minimize the effect of these unwanted interactions between radicals, we had to work at very low concentrations of peroxide and at rather low temperature, in order to decrease the stationary concentration of radicals as far as possible; consequently, we did not attempt to determine the ethyl affinities at 85°.

The anomaly encountered in the case of benzene cannot be easily explained. The reaction of radicals with benzene leads to the formation of some, presently undefined, product which seems to act as an efficient hydrogen donor, and its presence leads to the observed trend in k_6/k_5. Starting from these premises one can show that the "true" value of k_6/k_5 is obtained by extrapolating the observed values to zero concentration of benzene. Similar effects would be expected in experiments involving other aromatic compounds. However, since the latter compounds are more reactive than benzene and the mole fraction of isoöctane is essentially constant in pertinent experiments, the observed deviations should be negligible. Closer examination of data presented in Table I reveals indeed such minute deviations in the expected direction.

Intrinsic Reactivity of Ethyl Radicals.—The average values of k_6/k_5 listed in Table I are summarized in Table II. These values are recalculated on the assumption that the ethyl affinity of benzene is unity, an assumption which has no bearing whatever on the conclusions subsequently drawn and which is made for the sake of convenience only. The next two columns of Table II list the corresponding values of k_1/k_2 obtained for methyl radicals and the respective methyl affinities, all determined at 65°.[10] The plot of the log of ethyl affinities *versus* log of methyl affinities results in a straight line (see Fig. 1), vinyl acetate being the only compound which deviates from the observed regularity. The point representing benzene lies well on the line. However, if the ethyl affinity of benzene were obtained by extrapolating the experimental values to zero concentration of isoöctane, the point representing benzene would deviate from the line, leaving the relative positions of all the other points unchanged.

TABLE II

Compound	k_6/k_5	Ethyl affinity	k_1/k_2	Methyl affinity
Benzene	2.9	1	0.29	1
Biphenyl	11.0 ± 0.4	3.8	1.5	5.2
Naphthalene	100 ± 3	34.5	8.7	30
Phenanthrene	124 ± 3	43	10.7	37
Quinoline	182 ± 2	63	13.4	46
trans-Stilbene	1440 ± 40	496	109	376
Benzophenone	50 ± 1	17	4.2	14.5
Vinyl acetate	214 ± 3	74	37	130

It was explained in ref. 3 that the linear relationship represented by Fig. 1 should be interpreted as a proportionality between ΔE_{methyl} and ΔE_{ethyl}, *i.e.*

$$\Delta E_{\text{methyl}} = \alpha \Delta E_{\text{ethyl}}$$

In the latter equation ΔE_{methyl} represents differences in activation energies of reactions (1) for any two compounds A_i and A_k, while ΔE_{ethyl} represents the difference in activation energies of reactions (6) for the same two compounds A_i and A_k. The proportionality coefficient α measures the relative reactivity of radicals, and this entity is referred to as an intrinsic reactivity of a radical.[1,2,3] α is given by the slope of the straight line shown in Fig. 1, and in the present case $\alpha = 1$. We conclude, therefore, that

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[10] These values are taken from refs. 1 and 2. What is referred to in this paper as k_1/k_2 was originally denoted as $k11/k1$.

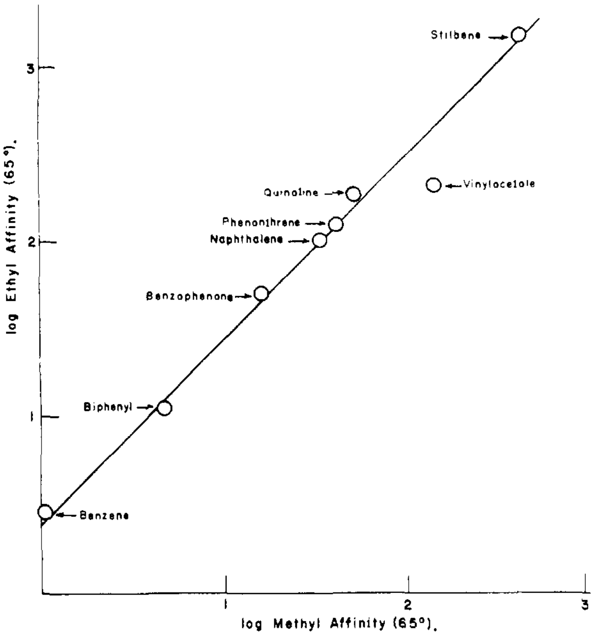

Fig. 1.

the intrinsic reactivities of methyl and ethyl radicals are identical.

Further Discussion of Results

In the preceding section, it was concluded that the intrinsic reactivities of methyl and ethyl radicals are similar. This might lead to the conclusion that $k_1 \approx k_6$ for any aromatic compound A. On the other hand, the data quoted in Table II indicate that on the average k_6/k_5 is approximately eleven times greater than k_1/k_2. It appears, therefore, that k_2 is approximately eleven times larger than k_5, and this point deserves further elaboration. Reactions (2) and (5) represent hydrogen abstraction from isoöctane by methyl and ethyl radicals, respectively. In these reactions a C–H bond has to be ruptured and the driving force arises from the energy gained in the formation of a new C–H bond. The C–H bond dissociation energy in methane is by about 3–4 kcal./mole greater than the C–H bond dissociation energy in ethane. In view of the symmetry of reactions (2) and (5), in both of which a C–H bond is broken and a C–H bond is formed, one would expect that one half of the difference in the exothermicities of these reactions would appear in the differences of the corresponding activation energies,[11] *i.e.*, $E_5 - E_2 = 1.5\text{–}2$ kcal./mole. Assuming that the corresponding A factors remain the same, we deduce that

$$k_2/k_5 \approx \exp(1.75/RT) \approx 13$$

On the other hand, reactions (1) and (6) represent an addition of a radical to an aromatic molecule. It was suggested[1,12] that the course of such a reaction is represented by an energy diagram as illustrated by Fig. 2. The repulsion curve represents the interaction between a radical and an aromatic molecule in its singlet ground state, while the attraction curve corresponds to the interaction between the same radical and the aromatic molecule in the excited triplet state. The depths of the attraction curves represent the dissociation energies of the A–R bonds, $R = CH_3$ or C_2H_5. It is plausible to expect that $D(\text{A–CH}_3)$ is greater than $D(\text{A–C}_2\text{H}_5)$. However, this difference should not affect the activation energy of the reaction if the shape of the repulsion curve and the slope of the attraction curve remain the same for methyl and ethyl radicals (see Fig. 2).

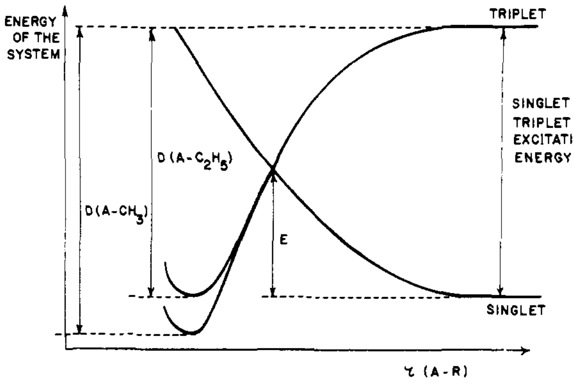

Fig. 2.

It was assumed earlier in this discussion that $A_5 \approx A_2$. This assumption can now be modified. Any difference between A_5 and A_2 would not affect our reasoning if the following plausible condition is fulfilled

$$A_5/A_2 \approx A_6/A_1$$

Finally, let us remark that the representation of the course of the addition reaction (1 or 6) in terms of diagram (2) emphasizes more the initial state of the system (*i.e.*, the separation between the attraction and the repulsion curves) than its final state (*i.e.*, the depth of the attraction curve). Obviously, for different compounds of type A one would expect different depths of the attraction curve, since the dissociation energies of the A–CH_3 (or $\text{A–C}_2\text{H}_5$) bonds should be affected by the nature of compound A. Nevertheless, the observed linear relation between the log of methyl affinities and the singlet–triplet excitation energies[12] indicates that the strength of the A–CH_3 bond is not an important factor in determining the rate of the addition reaction. The present results, *i.e.*, the comparison of methyl and ethyl affinities, stress this point again, and thus they can be considered as additional evidence in favor of the proposed representation of the course of the addition reaction.

In conclusion, we wish to thank the National Science Foundation for the generous support of this investigation.

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