composition are essentially the same in both phases, and that a change of solvent only slightly affects the rate of the decomposition. The rate of the primary decomposition of the following compounds was found to be affected only slightly by the nature of an inert solvent: benzoyl peroxide,[12] *t*-butyl perbenzoate,[13] and hexaphenylethane[14] (the latter reaction was investigated in 28 solvents). Unfortunately, neither of these reactions were studied in gaseous phase.

Recently, Alder and Leffler[15] investigated the effect of solvents on the rate of homolytic dissociation of phenylazotriphenylmethane. Analysis of their data shows again that the rates of the decomposition are only slightly affected by the nature of a solvent, although the apparent activation varies by about 4.5 kcal./mole. The approximate constancy of the rate constants demands a linear relation between activation energy and entropy of activation, and therefore it is not surprising that such a relation was found by the latter authors.

In conclusion, we would like to thank the National Science Foundation for financial support of this investigation.

[12] P. D. Bartlett and K. Nozaki, THIS JOURNAL, **68**, 1686 (1946); C. G. Swain, W. Stockmayer and T. Clarke, *ibid.*, **72**, 5426 (1950); C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

[13] A. T. Blomquist, THIS JOURNAL, **73**, 3408, 3412, 5546 (1951).

[14] K. Ziegler, P. Orth and K. Weber, *Ann.*, **504**, 131 (1933).

[15] M. G. Alder and J. E. Leffler, THIS JOURNAL, **76**, 1425 (1954).

SYRACUSE, N. Y.

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

The Kinetics of Decomposition of Acetyl Peroxide. III. The Reactions of Radicals Produced in the Decomposition

BY M. LEVY AND M. SZWARC

RECEIVED JUNE 9, 1954

A technique has been developed for determining quantitatively small amounts of methane, ethane and carbon dioxide produced in the thermal decomposition of dilute solutions of acetyl peroxide. It seems that in a diluted solution of isooctane or cyclohexane methyl radicals are converted quantitatively into methane and ethane, the latter being probably produced in a cage reaction. On the other hand, a considerable fraction of methyl radicals is "lost" in benzene solution, and it was shown that such a "loss" is due to the direct addition of methyl radicals to an aromatic molecule. Such a reaction seems to be characteristic for an aromatic compounds–radicals interaction. There is evidence that acetate radicals are more stable in solution of acetic acid or propionic acid than in solution of hydrocarbons. It is suggested that this increase in the stability is due to hydrogen bonding between the radical and the solvent. Finally, the decomposition has been studied in solution of fluorochemicals in a vain attempt to find a solvent which would be inert toward radicals.

This communication, denoted at Part III of the present series, is devoted to a discussion of elementary reactions involving the radicals produced by the thermal decomposition of diacetyl peroxide, and is based on experiments in which the rates of formation of carbon dioxide, methane and ethane were measured.

Experimental

Thoroughly evacuated solutions of acetyl peroxide (10 cc.) were sealed in a flask provided with a break seal. The flask was immersed in a heating bath, the temperature of which was kept constant within ±0.1°. At the end of a predetermined period of time, the flask was removed, its contents frozen immediately, and then analyzed with help of an apparatus shown schematically in Fig. 1. The reaction flask R is attached to a ground joint linked with trap T_1. The latter was cooled to $-115°$ using frozen ethyl bromide as a cooling agent. The whole apparatus was evacuated below 10^{-5} mm. Thereafter, the break seal was broken with the help of a magnetic hammer (M), and the contents of the flask were distilled over to Trap T_1. During the distillation, the two pumps (a mercury vapor pump and a Toepler pump) were simultaneously operating and consequently carbon dioxide, methane and ethane produced in the reaction were transferred to trap T_2 and storage section S. Blank runs have shown that this procedure enables one to separate quantitatively all these gases from the solvent.

Trap T_2 was cooled by liquid nitrogen, and thus the carbon dioxide and the ethane remained frozen. Therefore, the pressure in the system measured the amount of methane produced in the reaction. When the latter was determined, the liquid nitrogen bath was replaced by a solid carbon dioxide–acetone bath, and the increase in pressure measured, then the amount of $CO_2 + C_2H_6$ produced. Finally, the amount of CO_2 produced was measured by absorbing the latter by ascarite.

Results and Discussion

The experimental results are listed in Tables I, II and III. Inspection of these tables brings out the following points. For the decomposition, carried out in a diluted isoöctane or in cyclohexane solution at 65°, the ratio $(CH_4 + 2C_2H_6)/CO_2$ is unity within experimental error. This indicates that under these experimental conditions neither reaction (1) nor (2) takes place to any measurable extent.

$$CH_3{\cdot}COO + CH_3 \longrightarrow CH_3{\cdot}COOCH_3 \qquad (1)$$

$$CH_3 + (CH_3COO)_2 \longrightarrow CH_3{\cdot}COOCH_3 + CH_3{\cdot}CO_2 \qquad (2)$$

TABLE I

DECOMPOSITION OF ACETYL PEROXIDE IN ISOÖCTANE[a]

T, °C.	*M* × 10^3	Time, hr.	No. exper.	$\frac{2CO_2}{\text{peroxide decomp.}}$	$\frac{CH_4}{CO_2}$	$\frac{C_2H_6}{CO_2}$	$\frac{CH_4 + 2C_2H_6}{CO_2}$
64.9	9.5	1	1	1.05	0.776	0.115	1.005
64.9	9.5	2	8	0.95	.817	.077	0.971
64.9	9.5	4	2	.95	.873	.058	.989
64.9	9.5	8	1	.98	.770	.023	.816(?)
64.9	9.5	16	1	.82(?)	.840	.079	.998
64.9	9.5	32	1	.92	.800	.033	.866(?)
64.9	94	1	1	.85	.805	.036	.877
64.9	94	2	1	.83	.817	.035	.887
85.2	6	2	3	.86	.815	.045	905
85.2	11	2	2	.87	.790	.048	.886

[a] The values quoted in the last four columns represent average values if more than one experiment was performed.

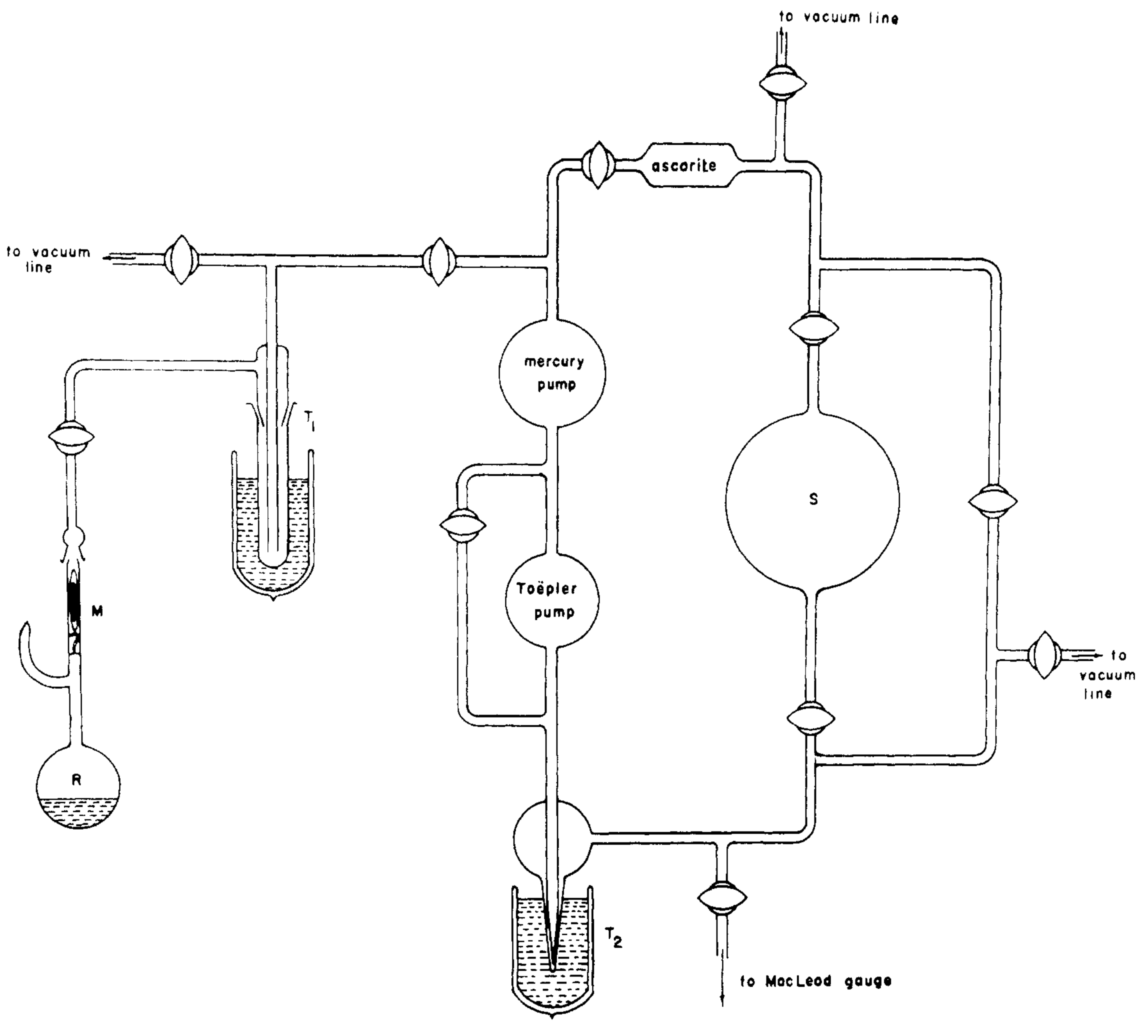

Fig. 1.

It seems that methyl radicals either react with solvent molecules abstracting hydrogen atoms, or they dimerize. These reactions can be represented either by equations 3 and 4

$$CH_3 + HR \longrightarrow CH_4 + R \quad (3)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad (4)$$

or by equations 5 and 6

$$CH_3{\cdot}COO + HR \longrightarrow CH_4 + CO_2 + R \quad (5)$$

$$2CH_3{\cdot}COO \longrightarrow C_2H_6 + 2CO_2 \quad (6)$$

In some experiments the ratio $2CO_2$/(decomposed peroxide) is definitely less than unity. We conclude, therefore, that some acetate radicals (or acetate groups) are lost through processes which do not produce gases. In this connection the following reactions should be considered

$$CH_3{\cdot}COO + HR \longrightarrow CH_3{\cdot}COOH + R \quad (7)$$

$$CH_3{\cdot}COO + R \longrightarrow CH_3{\cdot}COOR \quad (8)$$

$$(CH_3COO)_2 + R \longrightarrow CH_3{\cdot}COOR + CH_3COO \quad (9)$$

The literature survey shows that acetic acid was detected amongst the products of decomposition of acetyl peroxide and this observation indicates the occurrence of reaction 7. To obtain some idea about its extent, we decomposed to completion a 0.01 M solution of acetyl peroxide in isoöctane and titrated the resulting mixture with 0.01 M NaOH. The result has shown that not more than 1% of acetate radicals react according to equation 7.[1] Reaction 9 represents an induced decomposition, and the data presented in Part II seem to indicate that the induced decomposition is negligible for concentrations lower than 0.01 M. We conclude, therefore, that reaction 8 is the main cause for the loss of acetate radicals.

The existence of "free" acetate radicals in solutions has been demonstrated by the recent work of Calvin and his colleagues,[2] who showed that in acetic acid solution about 1% of acetate radicals exchange according to equation 10

$$CH_3{\cdot}COO + CH_3COOH \longrightarrow CH_3{\cdot}COOH + CH_3{\cdot}COO \quad (10)$$

The interaction between "free" acetate radicals might lead to reaction 11 or 12

$$2CH_3{\cdot}COO \longrightarrow CH_3{\cdot}COO{\cdot}CH_3 + CO_2 \quad (11)$$

$$2CH_3{\cdot}COO \longrightarrow CH_3{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}CH_3 \quad (12)$$

Reaction 12 should be distinguished from the "cage

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[1] The same result was obtained by Kharasch, although under different experimental conditions.

[2] A. Fry, B. N. Tolbert and M. Calvin, *Trans. Faraday Soc.*, **49**, 1444 (1953).

TABLE II

T, °C.	$M \times 10^3$	% decomp. (CO_2)	$\frac{2CO_2}{\text{decomp. peroxide}}$	$\frac{CH_4}{CO_2}$	$\frac{C_2H_6}{CO_2}$	$\frac{CH_4 + 2C_2H_6}{CO_2}$
			Cyclohexane			
64.9	59.8	3.35	0.96	0.81	0.072	0.96
64.9	59.8	12.6	.96	.81	.044	.90
64.9	88.9	12.7	.95	.83	.079	.99
84.9	9.75	54.5	.91	.81	.108	1.03
			Acetic acid			
64.9	9.35	6.1	0.885	0.75	0.048	0.85
64.9	9.35	12.0	.880	.74	.042	.82
64.9	91.5	5.25	.830	.75	.048	.84
64.9	91.5	5.35	.855	.76	.052	.86
64.9	91.5	8.1	.865	.74	.047	.84
84.9	9.5	50.4	.795	.76	.050	.86
84.9	9.5	50.6	.795	.74	.057	.86
			Propionic acid			
64.9	15.6	5.35	...	0.71	0.052	0.81
64.9	15.6	5.25	...	.74	.053	.85
85.2	15.6	52.6	...	.75	.052	.85
85.2	15.6	53.0	...	.75	.050	.85
			Toluene			
64.9	6.8	12.4	0.86	0.78	0.047	0.87
64.9	6.9	6.9	0.88	.67	.087	.84
64.9	7.1	13.9	0.91	.72	035	.79
64.9	66.3	14.5	1.01	.67	.020	.71
64.9	67.5	7.4	0.93	.65	.034	.72
64.9	67.5	13.9	0.90	.68	.028	.74
84.9	8.1	60.0	0.87	.66	.040	.74

TABLE III

DECOMPOSITION OF ACETYL PEROXIDE IN BENZENE

T, °C.	$M \times 10^3$	Time, hr.	% decomp. (CO_2)	$\frac{CH_4}{CO_2}$	$\frac{C_2H_6}{CO_2}$	$\frac{CH_4 + 2C_2H_6}{CO_2}$	k_{CO_2}[a] sec.$^{-1}$ $\times 10^5$
65.0	8.0	1	3.15	0.096	0.077	0.250	0.89
65.0	8.0	2	7.35	.095	.084	.263	1.05
65.0	8.2	2	7.65	.107	.051	.209	1.10
65.0	8.2	4	14.8	.118	.040	.298	1.07
65.0	8.0	8	27.1	.174	.026	.226	1.10
65.0	8 0	16	45.0	.167	.040	.247	1.02
65.0	8.0	32	69.0	.200	.029	.229	1.00
65.0	38.2	32	73.0	.288	.040	.367	1.11
65.0	38.2	32	73.8	.285	.020	.326	1.14
65.0	76.0	1	3.9	.162	.027	.216	1.09
65.0	76.0	2	18.0	.175	.039	.253	1.15
65.0	76.0	4	16.6	.225	.025	.274	1.18
65.0	76.0	8	29.5	.253	.021	.294	1.22
65.0	76.0	16	51.5	.293	.024	.340	1.26
65.0	76.0	16.25	50.5	.296	.025	.345	1.20
65.0	87.0	1	4.0	.186	.034	.254	1.12
65.0	87.0	2	8.4	.214	.034	.282	1.11
65.0	87.0	4	15.1	.267	.020	.308	1.12
85.2	8.6	2	62.7	.162	.038	.238	13.6
85.2	8.6	2	62.1	.163	.036	.235	13.4
65.0	37.9	133	97.0	.287	.036	.360	...

[a] k_{CO_2} denotes the unimolecular rate constant measured by the rate of formation of CO_2.

recombination" discussed in Part II. In a "cage recombination" the two radicals produced by the dissociation recombine before they have a chance to diffuse out of the cage. The rate of such a reaction is proportional to the concentration of "cages," *i.e.*, it is proportional to the first power of the concentration of the peroxide and independent of the stationary concentration of "free" acetate radicals. On the other hand, the rate of reaction 12 would be proportional to the square of the stationary concentration of acetate radicals and therefore approximately to the square of the concentration of the peroxide. Hence, the increase in the stationary concentration of acetate radicals favors reactions 11 and 12.

Inspection of the data obtained in reactions which proceed in solutions of acetic acid or propionic acid suggest that in these solvents the stationary concentrations of acetate radicals might be higher than in a solution of hydrocarbons. This is shown by two observations: the ratio $(CH_4 + 2C_2H_6)/CO_2$ is smaller than unity, which indicates that methyl acetate might be formed in the reaction (probably by reaction 11); furthermore, the first-order rate constant for the decomposition seems to *decrease* with *increasing* concentration of the peroxide (see the data given in Part II), which might be considered as an indication for reaction 12. We suggest that the increasing stability of acetate radical in acetic acid might be due to hydrogen bonding with the solvent. This suggestion gains further support from independent observations[3] which indicate that the first-order rate constants for the decomposition of some hydroperoxides decreases with increasing concentration of the peroxide if the reaction is carried out in a hydroxylic solvent. This phenomenon also might be caused by hydrogen bonding between OH or RO radicals and the hydroxylic solvent, with the consequent recombination leading to peroxide products.

Let us remark at this juncture that the stability of acetate radicals in acetic acid (or OH radicals in water) has been attributed wrongly to the reaction $CH_3COO + CH_3COOH \rightarrow CH_3COOH + CH_3COO$ (or $OH + H_2O \rightarrow H_2O + OH$). This explanation appears frequently in the literature.[4] Of course, the exchange does not affect the rate of any reaction involving the radical (not even the rate of their unimolecular decomposition), and thus it does not affect their stationary concentration.

Let us examine now the ratio of C_2H_6/CO_2. The amount of C_2H_6 formed in the decomposition is not too reproducible. Nevertheless, inspection of the data reveals the striking fact that the ratio of C_2H_6/CO_2 does not seem to be affected by the concentration of the peroxide and by the temperature. These observations indicate clearly that C_2H_6 is *not* formed in a reaction involving two free radicals, like reactions 4 or 6. It seems to originate from a cage reaction, or it represents a spontaneous decomposition of acetyl peroxide

$$(CH_3COO)_2 \longrightarrow C_2H_6 + 2CO_2 \qquad (13)$$

Distinction between these two alternatives is impossible, and perhaps even irrelevant, if one is concerned with reactions in solution. The real issue is this: does reaction 13 takes place in the gaseous phase, where the cage reaction is out of

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(3) V. Stannett and R. B. Mesrobian, THIS JOURNAL, **72**, 4125 (1950).

(4) W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, London, 1949, pp. 19, 139 and 143.

the question. Unfortunately, the work presented in Part I cannot provide any answer to this question.

The most striking evidence for the "cage" mechanism of formation of ethane is given in Table IV. Addition of quinone to the solution of peroxide in toluene causes a remarkable decrease in the amount of methane formed. However, the amount of ethane formed remains essentially unaltered. Methane is formed from CH_3 (or $CH_3{\cdot}COO$) radicals by the reaction

$$CH_3{\cdot} + HR \longrightarrow CH_4 + R{\cdot}$$

It appears, therefore, that quinone competes with the solvent for methyl radicals, the reaction with the former giving products other than methane. Since this reagent does not affect the rate of formation of ethane, the latter could not be produced from "free" radicals and must result from a "cage" reaction.

TABLE IV

$Ac_2O_2 = 2.5 \times 10^{-2}$ *M*, *T*, 65°

Concentration of quinone in toluene	C_2H_6/CO_2	CH_4/CO_2
None	0.06 (av. value)	0.74 (av.)
0.025	.058	.54
.050	.064	.37
.05	.077	.35
.05	.039	.37
.1	.045	.25
.2	.044	.14
.2[a]	.040	.08

[a] 2,6-Dichloroquinone used instead of quinone.

It is important to notice that the ratio C_2H_6/CO_2 for the reaction carried out in propionic acid is not greater than that obtained in a solution of acetic acid. This indicates that the reaction $CH_3{\cdot}COO + H{\cdot}O{\cdot}CO{\cdot}C_2H_5 \rightarrow CH_3{\cdot}COOH + C_2H_5{\cdot}COO$ is not important.[5] This conclusion is in agreement with Calvin's findings relevant to reaction 10.

We turn now to results obtained in benzene solutions. They show clearly that in this solvent some methyl radicals are lost by reactions which produce neither methane nor ethane. To clarify this point further, let us digress for awhile into a general discussion of reactions taking place between radicals and aromatic compounds.

In an interaction involving radicals and aromatic hydrocarbons, as *e.g.*, benzene, two reactions need be considered as the most probable primary processes: I, the hydrogen atom abstraction, represented by equation 14

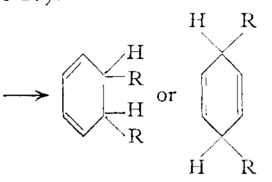
$$C_6H_6 + R{\cdot} \longrightarrow C_6H_5{\cdot} + R{\cdot}H{\cdot} \qquad (14)$$

and II, the radical addition reaction shown symbolically by equation 15

$$C_6H_6 + R{\cdot} \longrightarrow C_6H_6{\cdot}R{\cdot}\text{ complex} \qquad (15)$$

It appears[6] that the hydrogen atom abstraction prevails in reactions taking place in gaseous phase and it is favored by higher temperatures, while the radical addition predominates in reactions proceeding in solution. Of course, the primary complex, like $C_6H_6{\cdot}R$, cannot be the final product of the over-all reaction. It has to react further with radicals yielding eventually the final addition product (see *e.g.* equation 16) or the product of substitution (see equation 17).

Addition $C_6H_6{\cdot}R + R \longrightarrow$



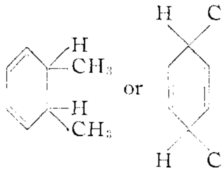
(16)

Substitution $C_6H_6{\cdot}R + R \longrightarrow C_6H_5{\cdot}R + H.R.$ (17)

The stoichiometry of the over-all reaction represented by equation 15 followed by 17 is identical with the stoichiometry of the process described by equation 14 followed by a recombination of phenyl and R radicals. Nevertheless, there are means for distinguishing between these two alternatives (see ref. 6).

On the other hand, reaction 15 followed by 16 leads to a different stoichiometry of the over-all process, and to entirely different products. Such products have been reported recently in publications by Magat and Bonême,[7] by Stockmayer and Peebles,[8] and by Marvel and Anderson.[9] These workers demonstrated that growing polymeric radicals may be added to aromatic hydrocarbons, the products of such reactions being copolymers which incorporate the aromatic compounds in their chains. Essentially the same conclusion has been drawn by Mayo[10] who studied the chain transfer reaction in bromobenzene. We believe that our work furnishes the evidence that methyl radicals are added to benzene, and that such a reaction accounts for the "loss" of methyl radicals.

A closer examination of our data clearly shows that the fraction of methane formed in the decomposition increases slightly with the progress of reaction. In our opinion, this increase indicates that addition products like, *e.g.*



react rapidly with methyl radicals giving substitution products and methane. It is important to notice, however, that even after a prolonged reaction (see the last result quoted in Table III) the relative amount of methane formed is still much smaller than that formed in the decomposition carried out in isoöctane or in cyclohexane.

It might be conceivable to assume that the interaction of methyl radicals with benzene produces toluene, and then the latter compound reacts rapidly with methyl radical giving an increasing amount of methane. To check this possibility we dissolved 7 mg. of toluene in 10 cc. of 8×10^{-3} molar solution of acetyl peroxide in benzene.

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[5] Such reaction would lead to the formation of ethyl radicals, and eventually to the formation of ethane.

[6] M. T. Jaquies and M. Szwarc, *Nature*, **170**, 312 (1952).

[7] M. Magat and R. Bonême, *Compt. rend.*, **232**, 1657 (1951).

[8] W. H. Stockmayer and L. H. Peebles, THIS JOURNAL, **75**, 2297 (1953).

[9] C. S. Marvel and W. S. Anderson, *ibid.*, **75**, 4600 (1953).

[10] F. K. Mayo, *ibid.*, **75**, 6133 (1953).

The amount of toluene introduced represents *the maximum* amount of toluene which could be produced in the reaction. This mixture was heated to 65° for one hour and thereafter analyzed. The amount of methane formed was the same as that produced under the same conditions and in the absence of toluene. Hence, the compound responsible for the formation of the additional quantity of methane cannot be toluene.

Bromination of the liquid which was obtained by decomposing the benzene solution of acetyl peroxide, furnished another piece of evidence supporting our mechanism of addition of methyl radicals to an aromatic hydrocarbon. Such a liquid has been shown to contain olefinic compounds. For example, decomposing 0.8 mmole of acetyl peroxide in 10 cc. of benzene (by heating this solution in vacuum to 65° for about 100 hours) produced a liquid which absorbed at 0° 1.5 cc. of 0.1 N solution of bromine. It was proved that neither the pure solvent, nor the unheated solution of acetyl peroxide in benzene, was absorbing bromine. Hence, an olefinic compound was produced by the decomposition of acetyl peroxide.

Investigation of the decomposition taking place in toluene solution shows again that the addition of methyl radicals to toluene occurs to some extent, although the reaction

$$C_6H_5\cdot CH_3 + CH_3 \longrightarrow C_6H_5\cdot CH_2 + CH_4 \quad (16)$$

competes efficiently with the addition process. Indeed, it will be shown in a later communication that the addition of methyl radicals to aromatic compounds is a quite general phenomenon, and the ability of an aromatic compound to add methyl radical (we propose to call this property the *methyl affinity* of an aromatic molecule) varies enormously. For example, the methyl affinity increases monotonously in a series: benzene, diphenyl, naphthalene, phenanthrene, anthracene and naphthacene, the last compound being about 8000 times as efficient as the first one.

Finally, we report briefly some experiments carried out in solutions of fluorochemicals.[11] Fluorochemicals were chosen as solvents which were expected to be inert toward radicals. The high C–F bond dissociation energy suggests that the reaction

$$C_nF_{2n+2} + R \longrightarrow C_nF_{2n+1} + RF$$

should not occur at the temperature of the experiments. Unfortunately, it appears that the fluorochemicals investigated contain a few extremely reactive C–H bonds, since a considerable amount of methane was produced in the decomposition. The presence of some C–H bonds in the fluorochemicals is evident from the fact that they are peroxidized (see Part II).

In conclusion we would like to thank the National Science Foundation for financial support of this investigation.

(11) The following fluorochemicals were investigated: perfluoromethylcyclohexane (Columbia Organic Chemicals Co.), perfluorodimethylcyclohexane (du Pont Co.), perfluorocyclic ether, probably $CF_3\cdot C_5F_9O$ (0–75 Minnesota Mining Co.).

SYRACUSE, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Donor–Acceptor Bonding. V. Studies of Some Molecular Addition Compounds of Stannic Chloride[1,2]

BY A. W. LAUBENGAYER AND WM. C. SMITH

RECEIVED JULY 19, 1954

The reactions of stannic chloride with a number of typical donor molecules have been studied as examples where the coordination of tin may be expected to increase to six. With $(CH_3)_3N$ and C_5H_5N white solid products having the empirical formulas $[(CH_3)_3N]_2\cdot SnCl_4$ and $(C_5H_5N)_2\cdot SnCl_4$ were obtained. BF_3 reacted with the former to give $(CH_3)_3N\cdot BF_3$. Ethyl alcohol and stannic chloride form a solid which upon recrystallization from ethyl alcohol or hot benzene gives well formed crystals having a composition corresponding to the empirical formula $(C_2H_5OH)\cdot(C_2H_5O)SnCl_3$. The data for this reaction are consistent with the assumption that unstable $(C_2H_5OH)_2\cdot SnCl_4$ forms initially but this then loses HCl, as suggested by Rosenheim. The infrared absorption spectrum of $(C_2H_5OH)\cdot(C_2H_5O)SnCl_3$ has been compared with those for gaseous and liquid ethyl alcohol. The formation of crystalline $[(C_2H_5)_2O]_2\cdot SnCl_4$ has been confirmed. This compound was purified by vacuum sublimation and studied in detail. It is reversibly dissociated in benzene. Extended vapor pressure–temperature measurements for the substance have been made and vapor density data indicate virtually complete dissociation of the complex in the vapor phase. Powder X-ray diffraction patterns have been recorded for all the complexes. The possible structures of these complexes of tin are considered.

Introduction

The conditions favoring the formation of molecular addition compounds and the important consequences of the donor–acceptor bond involved have been summarized in the first paper of this series.[3] Those complexes involving donor and acceptor molecules in a 1:1 ratio have been the subject of particularly thorough investigation. Very little is known, however, about reactions in which two donor molecules combine with a given acceptor molecule, and for this reason a study of this type of system was chosen for investigation.

Stannic chloride was selected as the acceptor molecule because of its recognized ability to attain a coördination number of six, as in the chlorostannate ion, $SnCl_6^=$. The structural features of such a donor–acceptor molecule offer interesting possibilities because of the opportunity for *cis*-

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(1) Paper IV of this series, A. W. Laubengayer and C. F. Condike, THIS JOURNAL, **70**, 2274 (1948).

(2) Based upon a thesis submitted by Wm. C. Smith to the Faculty of Cornell University in partial fulfillment of the requirements for the M.S. degree, 1951.

(3) A. W. Laubengayer and G. R. Finlay, THIS JOURNAL, **65**, 884 (1943).