Loss of hydrogen and volatile compounds is accompanied by a loss in weight of the sample. Likewise, as the supply of these gases is decreased by increased cross-linking and unsaturation, the amount of gas evolved per given irradiation dose increment was observed to decrease. For example, the evolution of hydrogen decreased from 106 μ per million roentgen when the sample was first irradiated to 86 μ per million roentgen after the sample had absorbed an accumulated dose of 1037 $\times 10^6$ roentgen. The corresponding decrease in volatile compounds was from 30 to 12 μ per million roentgen. The total weight decrease was from 0.1988 to 0.1947 g.

Cross-linking Efficiency.—If it is assumed that each hydrogen molecule evolved is indicative of one C–C cross-link, then it is possible from the above hydrogen data to calculate the concentration of cross-links and the efficiency of the irradiation in producing cross-links. The initial pressure change corresponds to a loss of 2×10^{-6} g. of hydrogen, or a decrease of about 0.007% of the available hydrogen. The concentration of cross-links computed from this would be $C = 3.33 \times 10^{18}$ per cubic centimeter. The efficiency of the irradiation in producing cross-links is defined as the concentration C, divided by the number of electrostatic charges, or ion pairs, per cubic centimeter of polymer produced by the irradiation. In the case of the above concentration which corresponds to an irradiation dose of 10^6 roentgen, the efficiency is found to be equal to 1.87. This is in agreement with other values as determined from tensile and swelling data.[7] The efficiency of production of cross-links decreased with increasing amounts of accumulated irradiation. The decrease as determined from the above hydrogen data was from the initial value of 1.87 to 1.51 after the sample had received an accumulated dose of 1037 $\times 10^6$ roentgen.

[7] E. J. Lawton, J. S. Balwit and A. M. Bueche, *Ind. Eng. Chem.*, in press.

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The Addition of Methyl Radicals to Benzene

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In an interaction involving radicals and aromatic hydrocarbons, as *e.g.*, benzene, two reactions need to be considered as the most probably primary processes: I, the hydrogen atom abstraction, represented by equation 1

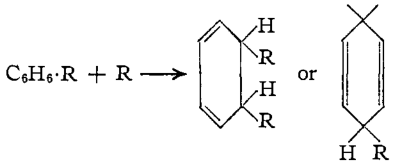
$$C_6H_6 + R\cdot \longrightarrow C_6H_5\cdot + R{\cdot}H \qquad (1)$$

and II, the radical addition reaction, shown symbolically by equation 2

$$C_6H_6 + R\cdot \longrightarrow C_6H_6R\cdot \text{ complex} \qquad (2)$$

It appears[1] 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 overall reaction. It has to react further with radicals, yielding eventually the final addition product (see *e.g.*, equation 3) or the product of substitution (see equation 4).

addition



(3)

substitution

$$C_6H_6{\cdot}R + R \longrightarrow C_6H_5{\cdot}R + H{\cdot}R \qquad (4)$$

The stoichiometry of the over-all reaction represented by equations 2 followed by (4) is identical with the stoichiometry of the process described by equation 1 followed by a recombination of phenyl and R radicals. Nevertheless, there are means for distinguishing between these two alternatives (see ref. 1).

On the other hand, reactions (2) followed by (3) lead 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,[2] by Stockmayer and Peebles,[3] and by Marvel and Anderson.[4] 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[5] who studied the chain transfer reaction in bromobenzene. Our present work furnishes the evidence that methyl radicals are added to benzene, and the relevant observations are described in this communication.

Experimental

Methyl radicals were generated by the thermal decomposition of acetyl peroxide. The compound was synthesized by the conventional method described, *e.g.*, in a paper by Price and Morita,[6] and it was purified by crystallization. Most of our experiments were carried out in solutions concentration of which varied from 7×10^{-2} molar to 4×10^{-3} molar and at a temperature of 65.0°. The investigated samples of solution were deaerated thoroughly in a special glass reaction vessels, and then immersed in a bath maintained at a temperature constant to ±0.1°. At the end of a predetermined period of time the samples were removed from the bath, frozen in acetone–solid carbon dioxide mixture and analyzed. The method of analysis[7] enables us to determine the amounts of carbon dioxide, methane and ethane, produced in the reaction, while the amount of undecomposed peroxide was determined by iodometric titration. The reliability of our analytical procedure was checked by special blank runs and it was found entirely satisfactory. The decomposition experiments were carried out in benzene, in cyclohexane, and in isoöctane. All these solvents were carefully purified.

Results

The decomposition of acetyl peroxide in isoöctane or in cyclohexane solution yielded carbon dioxide,

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[1] M. T. Jaquiss and M. Szwarc, *Nature*, **170**, 312 (1952).

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

[3] W. H. Stockmayer and L. H. Peebles, THIS JOURNAL, **75**, 2279 (1953).

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

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

[6] C. C. Price and H. Morita, *ibid.*, **75**, 3686 (1953).

[7] The details of our analytical methods as well as the full account of this work will be published in a later communication.

methane and comparatively small quantities of ethane. Table I gives few representative examples of our results which indicate that the formation of each mole of carbon dioxide is accompanied by the formation of one mole of methyl radicals, which eventually yield methane or ethane.

The progress of the decomposition was measured both by titrating the undecomposed peroxide, and by determining the amount of carbon dioxide formed. The data, listed also in Table I, show that the decomposition obeys first-order kinetics. The first-order rate constants, computed on the basis of peroxide titration, are slightly higher than those calculated from the amount of carbon dioxide formed. This small difference probably indicates that a small amount of cyclohexyl or isoöctyl acetate is formed during the process.

TABLE I

DECOMPOSITION OF ACETYL PEROXIDE AT 65.0°

Cyclohexane solvent

Concn., mmoles/cc. × 10^3	8.0	11.8	29.5	75.8
$k \times 10^2$, hours^{-1}	3.21	3.18	3.38	3.49

Gas Analysis

Concn., mmoles/cc. × 10^3		59.8	59.8	88.5
Time, hr.		1	4	4.1
Millimoles × 10^2	CO_2	3.75	14.4	21.6
	CH_4	3.03	11.7	17.9
	C_2H_6	0.27	0.64	1.70
$(CH_4 + 2C_2H_6)/CO_2$		0.955	0.90	0.985
$k_{CO_2} \times 10^2$, hr.		3.19	3.19	3.16

Isoöctane solvent

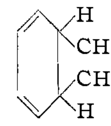
Concn., mmoles/cc. × 10^3	7.73	82.7
$k \times 10^2$, hours^{-1}	3.37	3.87

Gas analysis

Concn., mmoles/cc. × 10^3		9.35	94.0
Time, hr.		4	1
Millimoles × 10^2	CO_2	2.10	6.45
	CH_4	1.92	5.20
	C_2H_6	0.09	0.23
$(CH_4 + 2C_2H_6)/CO_2$		1.00	0.89
$k_{CO_2} \times 10^2$, hr.		3.03	3.18

On the other hand, the decomposition carried out in benzene solution yielded the anticipated amount of carbon dioxide but only a small quantity of methane and still smaller amount of ethane. We dissolved the relevant quantities of methane and ethane in benzene, and proved that our analytical procedure is capable to determine these products in a very satisfactory manner. Hence, we had to conclude that methyl radicals are consumed in this solvent by an addition process represented by equation 2, followed by reactions which are essentially similar to those described by equation 3.

The results of our experiments are listed in Table II. Examination of this table shows clearly 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 II) 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 suggestion we dissolved 7 mg. of toluene in 10 cc. of 8 × 10^{-3} molar solution of acetyl peroxide in benzene. The amount of toluene introduced represents *the maximum* amount of toluene which could be produced in the reaction. This mixture was heated to 65°

TABLE II

DECOMPOSITION OF ACETYL PEROXIDE IN BENZENE AT 65.1°

Concn., mmole/cc. × 10^3	Time, hr.	CO_2 in mmoles × 10^2	CH_4	C_2H_6	$\frac{CH_4 + 2C_2H_6}{CO_2}$	$\frac{CH_4}{CO_2}$	$\frac{CO_2}{\text{Peroxide}}$	$k_{CO_2} \times 10^2$ hours^{-1}
8.0	1	0.48	0.047	0.037	0.250	0.096	0.030	3.04(?)
8.0	2	1.125	0.107	.095	.264	.095	.070	3.65
8.0	8	4.14	0.75	.105	.232	.174	.259	3.74
8.0	16	6.73	1.12	.270	.247	.167	.420	3.40
8.0	32	10.5	2.10	.300	.257	.200	.657	3.34
38.2	32	53.1	15.3	2.1	.367	.288	.695	3.70
38.2	32	53.7	15.3	1.1	.326	.285	.703	3.78
76.0	1	5.55	0.90	0.15	.216	.162	.037	3.75
76.0	1	5.70	....	.15	...	...	.038	3.84
76.0	2	11.6	2.03	.45	.253	.175	.076	3.98
76.0	4	24.0	5.4	.60	.274	.225	.158	4.03
76.0	8	42.7	10.8	.90	.294	.253	.281	4.13
76.0	16	75.0	22.0	1.80	.340	.293	.490	4.20
76.0	16.25	73.0	21.6	1.80	.345	.296	.480	4.03
37.9	133	70.0	20.2	2.5	.360	.287	.925	..

The rate of decomposition measured by the iodometric titration was found to be 3.80 × 10^{-2} h.$^{-1}$ at the initial concentration of 8 × 10^{-3} millimoles of peroxide per cc. However, at concentration of 87 × 10^{-3} millimoles/cc. the rate of decomposition seems to decrease with time of reaction from the initial value of 4.2 × 10^{-2} h.$^{-1}$ to about 3.4 × 10^{-2} h.$^{-1}$ at 75% decomposition.