The light scattering method of studying hapten–antibody equilibria described here stands midway between the dialysis equilibrium method, which permits a study of only monovalent-hapten systems, and the Singer–Campbell method which provides information on the equilibrium involved in the first and second antigen–antibody complex (see equation 10). This method has some advantage over the equilibrium dialysis method in that it permits investigation of the effect of the spatial arrangement of two haptenic groups on the bond formation and provides for the possibility of a study of reaction rates in which the initial and final states are clearly defined. The Singer–Campbell method has the distinct advantage of being applicable to protein antigens, but in that case an estimate of the valency of the antigen is required. In their method the equilibrium concentration of free antigen is determined by electrophoretic or ultracentrifugal resolution, and systems may be encountered in which this is made difficult by especially rapid re-equilibration among the species present in an antigen–antibody solution. The light scattering method, involving no disturbance of the equilibrium state of the solution, does not suffer from this possible limitation. While it is likely that other complications would arise in applying the light scattering method to protein antigen–antibody systems in a quantitative manner, such an effort appears nevertheless worthwhile.

Acknowledgments.—We are glad to acknowledge the gift of the haptens used in this work from Drs. D. H. Campbell and D. Pressman. We are indebted to Dr. B. M. Pitt for help in the antibody purifications, particularly for the suggestion leading to the development of Procedure B. In addition we wish to thank Dr. S. J. Singer for permission to quote the results of some of his measurements made at Yale University.

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The Role of Solvents in the Decomposition of Propionyl and Butyryl Peroxides

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The decomposition of propionyl and butyryl peroxides in a variety of solvents was investigated. It was shown that the primary reaction involves the rupture of the O–O bond and formation of R·CO_2 radicals which decarboxylate rapidly, yielding the corresponding hydrocarbon radicals. It was demonstrated that butane formed in the decomposition of propionyl peroxide results from a cage recombination of ethyl radicals and that disproportionation as well as recombination takes place in the "cage." The decomposition in hydrocarbon solvents was contrasted with the decomposition proceeding in polar solvents. The role of solvents in the decomposition was discussed and the ionic mode of decomposition was considered. The radical induced decomposition was investigated, and it was demonstrated that this reaction is initiated mainly by solvent radicals.

Investigation of the pyrolysis of gaseous propionyl and butyryl peroxides[1] demonstrated that these compounds decompose in a unimolecular fashion, the rates being determined by the ease with which the respective O–O bonds are ruptured

$$R\cdot CO\cdot O\cdot O\cdot CO\cdot R \longrightarrow 2R\cdot CO_2 \qquad (1)$$

It was shown that for R = CH_3, C_2H_5 or n-C_3H_7, the activation energies and the frequency factors of reactions described by equation 1 are nearly constant, namely

	E, kcal./mole	$A \times 10^{14}$, sec.$^{-1}$
CH_3	29.5	1.8
C_2H_5	30.0	2.5
n-C_3H_7	29.6	1.9

In view of the similarity in behavior of these compounds in gaseous decomposition, the kinetics of their decomposition in a variety of solvents has been studied in an attempt to shed more light on the nature of factors which govern the rates of chemical processes taking place in solution.

Experimental and Results

Propionyl and butyryl peroxides were prepared and purified by the method described previously.[1] The following solvents were used: spectroscopically pure isoöctane, analytically pure benzene, toluene, acetic acid and acetic anhydride and chemically pure n-hexane, 1,4-dioxane, nitrobenzene and benzonitrile. All these solvents were distilled prior to use through an efficient Todd column, the middle fraction being collected. 1,4-Dioxane was distilled over calcium hydride in order to destroy the peroxides originally present in this solvent. The absence of peroxides in all the other solvents was demonstrated.

Two techniques were used in investigating the kinetics of the decomposition. One series of experiments was conducted with deaerated solutions of peroxides, sealed in glass ampoules and heated for a predetermined period of time at a desirable temperature. The temperature bath was controlled within ±0.1°, the thermometers used were calibrated by means of a standard thermometer calibrated by The National Bureau of Standards. At the end of the required period of time, the ampoules were withdrawn from thermostatic bath, cooled rapidly by immersion in the solid carbon dioxide–methanol bath, and then their contents were analyzed for undecomposed peroxide. The iodometric technique described by Wagner, Smith and Peters[2] was used in analysis of all solutions with the exception of those con-

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

(2) C. D. Wagner, R. H. Smith and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976 (1947).

taining nitrobenzene. The yellow color of the latter solvent interferes with the determination of the end-point of titration, and thus the nitrobenzene solutions were analyzed by the electrometric technique described by Abrahamson and Linschitz.[3]

The results proved that the rate of decomposition is given correctly by the first-order law, even at a high % of decomposition. Plots of logarithms of concentration against time resulted in straight lines, and the first-order rate constants, computed from the respective slopes, are listed in Tables I and II. The activation energies calculated from the results obtained at lowest concentrations are listed in Table III, which also includes, for the sake of comparison, the results obtained from studies of the decomposition of acetyl peroxide.[4]

TABLE I

DECOMPOSITION OF PROPIONYL PEROXIDE

Solvent	Concn. of peroxide $\times 10^3$, M	First-order rate constants $k \times 10^6$, sec.$^{-1}$ At 65.0°	At 85.0°
Gas phase	...	1.00	16
Isoöctane	1.09	0.98	14.4[a]
	2.45	0.93	15.1[a]
	7.6	1.08	17.2[a]
	14.5	1.14	...
	75.0	1.43	20.8[a]
n-Hexane	7.6	1.48	17.1
	74.6	1.52	17.3
Benzene	1.1	1.90	24.0
	7.7	1.86	24.0
	76.4	2.06	29.1
Toluene	7.7	1.83	24.0
	76.0	1.90	26.8
Glacial acetic acid	7.0	3.8	43
	77.7	4.0	50
Acetic anhydride	7.9	3.5	45
	79.0	3.0	50
Dioxane	7.4	4.5	45
	74.0	5.5	52
Benzonitrile	7.9	3.9	51
	76.7	3.5	50
Nitrobenzene	7.3	3.7[b]	41[b]
	70.0	4.2[b]	

[a] These experiments were carried out at 86.5°. [b] Titration of peroxide was carried out by using a potentiometric technique.

TABLE II

DECOMPOSITION OF BUTYRYL PEROXIDE

Solvent	Concn. of peroxide $\times 10^3$, M	First-order rate constant $k \times 10^5$, sec.$^{-1}$ At 65.0°	At 85.0°
Gas phase	..	1.6	20.0
Isoöctane	7.7	1.11	15.6
	61.7	1.36	18.7
n-Hexane	7.4	1.14	15.3
	66.4	1.35	17.2
Benzene	7.3	2.24	30.2
	64.8	2.11	33.1
Toluene	7.0	2.14	28.7
	64.1	2.00	30.0
Glacial acetic acid	7.7	4.7	56
	69.4	5.0	63
Acetic anhydride	7.4	4.3	55
	65.0		58.5
Dioxane	7.7	4.6	46
	65.1	5.4	58
Benzonitrile	6.7	4.3	58
	70.0	4.0	58

TABLE III

Solvent	Acetyl peroxide E, kcal./mole	$k \times 10^5$, sec.$^{-1}$ at 65°	Propionyl peroxide E, kcal./mole	$k \times 10^5$, sec.$^{-1}$ at 65°	Butyryl peroxide E, kcal./mole	$k \times 10^5$, sec.$^{-1}$ at 65°
Gas phase	29.5	1.8	30.0	1.00	29.6	1.60
Isoöctane	32.2	0.94	31.2	0.98	31.9	1.11
n-Hexane	..	..	29.6	1.48	31.4	1.14
Benzene	32.3	1.10	30.9	1.90	31.4	2.24
Toluene	32.0	1.15	31.1	1.83	31.2	2.14
Acetic acid	30.2	1.00	29.4	3.8	29.9	4.7
Acetic anhydride	..	..	30.8	3.5	30.7	4.3
Dioxane	..	..	27.9	4.5	27.8	4.6
Benzonitrile	..	..	31.2	3.9	31.4	4.3
Nitrobenzene	..	..	28.9	3.7	..	..

The data collected in Tables I and II show that the first-order rate constants increase at higher concentration of peroxides. Such behavior indicates the occurrence of an induced decomposition and, assuming stationary concentration of radicals, one may derive the following expression for the "first-order" rate constant

$$k_{\text{exp}} = k_1 + k_{\text{ind}}(k_1/k_2)^{1/2} \times (\text{peroxide})^{1/2}$$

In this expression k_1 denotes the "true" first-order rate constant characterizing the primary, unimolecular decomposition of the peroxide; k_2 denotes the rate constant for the recombination (or disproportionation) of radicals and k_{ind} represents the rate constant of the induced decomposition, *i.e.*

$$\text{R}\cdot + \text{peroxide} \longrightarrow \text{products} + \text{R}\cdot$$

The values of k_{exp}, determined from the kinetics of decomposition of propionyl peroxide in isoöctane solution at 65°, are plotted *versus* the square-root of concentration. The resulting straight line is shown in Fig. 1, its slope gives $k_{\text{ind}}(k_1/k_2)^{1/2}$, while the intercept gives k_1. For the sake of comparison we included in Fig. 1 a similar plot characteristic for the decomposition of acetyl peroxide in the same solvent and at the same temperature.[5] It is interesting to notice that the k_1 values are very close for both peroxides, namely, 0.92×10^{-5} sec.$^{-1}$ for propionyl peroxide and 0.88×10^{-5} sec.$^{-1}$ for acetyl peroxide. On the other hand, $k_{\text{ind}}/\sqrt{k_2}$ for propionyl peroxide is 2.5 times greater than for acetyl peroxide. Assuming that the k_2 are the same in both cases,[6] we conclude that in isoöctane solution propionyl peroxide is 2.5 times more susceptible to induced decomposition than acetyl peroxide. This effect might result from the presence of ethyl radicals, which live longer than methyl radicals and might be more reactive than solvent radicals.

The data collected in Tables I and II show clearly that the extent of the induced decomposition varies greatly with the nature of solvent, *e.g.*, very little of induced decomposition is observed in toluene or benzene solution. This indicates a considerable contribution of solvent radicals to the induced decomposition, and this point will emerge even clearer from discussion of the results obtained in other series of experiments. In a few cases the experimental rate constants seem to increase at lower concentration of peroxide. No plausible explanation of this anomaly can be offered at this stage.

The results listed in Table III show how strikingly similar are the rate constants and the activation energies of the decomposition of propionyl and butyryl peroxides in all these different solvents. It appears that the same factor, *i.e.*, the homolytic rupture of the O–O bond, determines the rates of decomposition in hydrocarbon solutions and in gaseous phase. On the other hand, it seems that some additional mode of decomposition is operative in polar solvents, since

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[3] E. W. Abrahamson and H. Linschitz, *Anal. Chem.*, **24**, 1355 (1952).

[4] M. Levy, M. Steinberg and M. Szwarc, THIS JOURNAL, **76**, 5978 (1954).

[5] The data are taken from reference 4.

[6] k_2 refers to the bimolecular interaction of radicals, namely, R + R → products. It appears that the recombining radicals R are composed mainly of solvent radicals, thus essentially the same recombination processes take place in the decomposition of either peroxide.

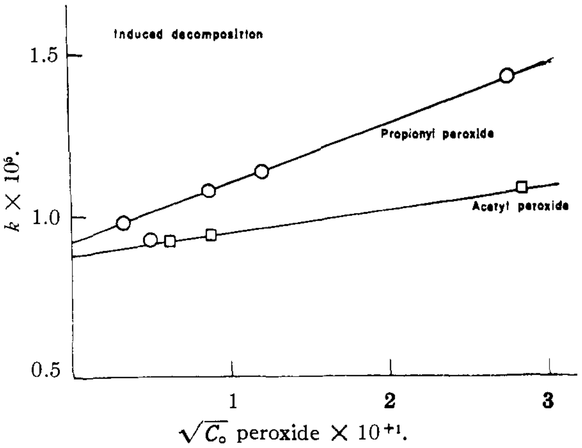

Fig. 1.

in the latter solutions the rates of the reaction are definitely higher.

To get further insight into the mechanism of the decomposition and the role of solvents, the products of the reaction were isolated and quantitatively determined.. Technical difficulties prevented us from studying products of the decomposition of butyryl peroxide and therefore only the products of decomposition of propionyl peroxide were investigated quantitatively. The latter contain carbon dioxide, C_2 hydrocarbons (ethane and smaller quantities of ethylene), butane, propionic acid and its esters. Quantitative determinations of the gaseous products was accomplished in an apparatus shown in Fig. 2, and the following procedure was adopted in the analysis.

Experimental (Gas Analysis)

Deaerated solutions of propionyl peroxide (about 10 cc.) were sealed in glass ampoules equipped with break seals. Each ampoule was heated for a predetermined period of time at the desired temperature, the reaction was then interrupted by cooling the contents to −80° and the ampoule (R) attached to the apparatus through a ground joint linked to Trap T_1. The whole apparatus was evacuated until the pressure dropped below 10^{-5} mm., and then the break seal was crushed by means of a magnetic hammer while stopcock S_1 was closed and trap T_1 kept in liquid nitrogen. The contents of the ampoule is distilled into trap T_1, containing an inner finger cooled by solid carbon dioxide–methanol mixture. After completion of the transfer stopcock S_1 was opened and liquid nitrogen removed from the outside of trap T_1. At that time traps T_3 and T_4 were cooled by liquid nitrogen, trap T_2 by solid carbon dioxide–methanol mixture and the mercury vapor pump P_1 and the Toepler pump P_2 put into operation. The gases present in trap T_1 then distil over into further parts of the apparatus, while the solvent gently boils and refluxes on the cooled finger. Such a reflux is essential for the quantitative removal of butane which is easily retained by solvents used in the reaction. The non-condensable gases (*e.g.*, methane or nitrogen) were pumped into storage bulb S, their quantity[7] determined manometrically and thereafter they were pumped out of the system. The condensable gases present in trap T_3 were separated by low temperature distillation.[8] Ethane and ethylene distilled first and were transferred by pumps P_1 and P_2 into the storage bulb. At this stage of operation trap T_4 was cooled to −80° only to permit a manometric determination of their quantities. After determining the pressure of C_2 hydrocarbons, these gases were in turn pumped out of the system, and then carbon dioxide was distilled and transferred into the storage bulb. This gas always contained small amounts of butane and, therefore, its quantity was determined by absorbing it by ascarite (this procedure is described by Levy and Szwarc).[10] Finally, butane was transferred into the storage bulb and its quantity determined manometrically. The reliability of the method described here was ascertained by special blank experiments.

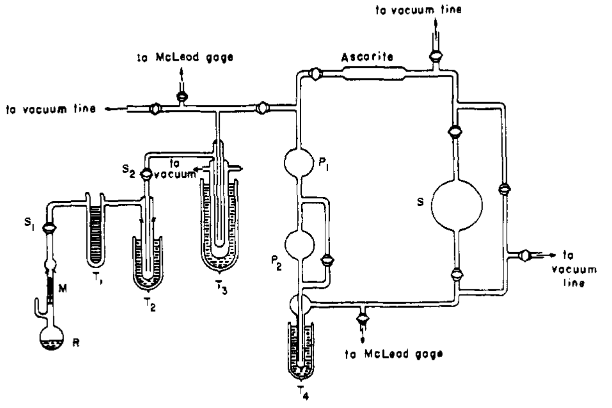

Fig. 2.

The results obtained in this series of experiments are given in Table IV. The second column, headed C_2H_6/CO_2, gives the ratio of C_2 hydrocarbons formed in the reaction (*i.e.*, ethane + ethylene) to carbon dioxide, "total" denotes ethane + ethylene + 2 butane, *i.e.*, the total amount of ethyl radicals composing the hydrocarbons formed by the decomposition. The % of decomposition is calculated from the amount of carbon dioxide formed, assuming $2CO_2$ to be equivalent to one molecule of the peroxide decomposed, and this % of decomposition is used in calculating the unimolecular rate constants k_{CO_2} given in the last column of Table IV.

Discussion

The decomposition of propionyl and butyryl peroxides is initiated by reaction (1) followed by a rapid decarboxylation of propionate (or butyrate) radicals.[11] Radicals R formed in reaction (3)

$$R{\cdot}CO_2 \longrightarrow R + CO_2 \qquad (3)$$

react with solvent abstracting hydrogen atoms; the latter reaction accounts for the ethane formed in the decomposition of propionyl peroxide. The formation of butane observed in the decomposition of propionyl peroxide may be attributed to a recombination process

$$2C_2H_5 \longrightarrow C_4H_{10} \qquad (4)$$

However, the data presented in Table IV leave no doubt that reaction (4) does not result from a bimolecular recombination process involving free radicals which lost their identity but that it results from a cage recombination involving the two radicals formed from a single molecule of propionyl peroxide. While the bimolecular reaction is kinetically second order in respect to the stationary concentration of radicals, the cage recombination is first order in respect to the peroxide. Now, the data listed in the first part of Table IV show clearly that in isoöctane solution the fraction of ethyl radicals forming butane (*i.e.*, C_4H_{10}/CO_2) remains constant when the concentration of the peroxide varies by more than a factor of ten (at 65° and at concentration 0.121×10^{-2} *M*, the average value of C_4H_{10}/CO_2 is 0.133 ± 0.004, while at concentration $1.25–1.45 \times 10^{-2}$ *M*, it is found to be 0.141 ± 0.017). Furthermore, approximately the same value of C_4H_{10}/CO_2 has been found for the

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[7] The non-condensable gases were present in quantities lesser than 1% of carbon dioxide formed in the reaction.

[8] Actually trap T_3 is a low temp. distn. col. described by LeRoy.[9]

[9] D. J. LeRoy, *Can. J. Research*, **B28**, 492 (1950).

[10] M. Levy and M. Szwarc, THIS JOURNAL, **77**, 5493 (1955).

[11] Thermochemical data (Jaffe, Prozen and Szwarc in course of publication) prove that the decarboxylation described by equation 3 is *exothermic* to an extent of about 12–14 kcal./mole for R = CH_3, C_2H_5 or *n*-C_3H_7.

TABLE IV

Concn. peroxide $\times 10^2$, M	C_2H_6/CO_2[a]	C_4H_{10}/CO_2	Total[a]/CO_2	% Decomp. (2 hr.)	k_{CO_2} · 10^5, sec.$^{-1}$
Solvent isoöctane, temperature 65°					
0.121	0.597	0.139	0.875	36.9 (14 hr.)	0.91
.121	.601	.130	.861	36.7 (14 hr.)	.91
.121	.608	.131	.870	66.3 (37 hr.)	.82
Av.	.602 ± 0.004	.133 ± 0.004	.869 ± 0.005	...	.88
1.25	.563	...	...	7.00	1.00
1.25	.570	...	...	6.95	1.00
1.25	.578	...	...	7.10	1.03
1.25	.554	.160	.871	7.38	1.06
1.25	.565	.166	.897	7.32	1.05
1.25	.571	.171	.913	7.00	1.00
1.25	.555	.155	.865	7.30	1.05
1.21	.551	.131	.813	10.6 (3 hr.)	1.05
1.21	.568	.150	.868	7.12	1.03
1.45	.554	.132	.818	7.11	1.03
1.45	.544	.122	.788	7.13	1.03
1.45	.562	.123	.808	6.87	0.99
1.45	.557	.124	.841	7.03	1.01
1.45	.557	.120	.797	7.13	1.03
Av.	.561 ± 0.007	.141 ± 0.017	.844 ± 0.036	...	1.03
81.6	.584	.120	.824	8.2	1.19
81.6	.583	.124	.831	8.3	1.20
Solvent isoöctane, temperature 85°					
0.125	0.551	0.142	0.836	56.1 (1.5 hr.)	14.5
.125	.552	.136	.824	56.4 (1.5 hr.)	15.2
Av.	.552	.139	.830	...	14.9
0.50	.548	.126	.800	50.2 (1.5 hr.)	12.9
.50	.550	.145	.840	49.7 (1.5 hr.)	12.7
Av.	.549	.135	.820	...	12.8
1.25	.527	.131	.789	51.3 (1.5 hr.)	13.3
1.25	.522	.131	.784	51.3 (1.5 hr.)	13.3
1.25	.522	.123	.768	50.6 (1.5 hr.)	13.0
1.25	.530	.123	.776	51.6 (1.5 hr.)	13.4
1.25	.525	.125	.775	50.5 (1.5 hr.)	13.0
Av.	.525 ± 0.003	.126 ± 0.003	.778 ± 0.006	...	13.2
Solvent, benzene, temperature 65°					
0.142	0.108	0.128	0.364	55.2 (12 hr.)	1.86
.142	.109	.105	.339	55.2 (12 hr.)	1.86
1.42	.123	.124	.371	9.7 (1.5 hr.)	1.89
1.42	.125	.124	.373	9.6 (1.5 hr.)	1.86
Solvent toluene, temperature 65°					
0.145	0.474	0.156	0.786	56.8 (12 hr.)	1.94
.145	.460	.151	.762	56.2 (12 hr.)	1.91
1.45	.450	.150	.750	9.7 (1.5 hr.)	1.89
1.45	.443	.158	.759	9.8 (1.5 hr.)	1.90
Solvent acetic acid, temperature 65°					
0.146	0.464	0.134	0.732	40.4 (6 hr.)	2.30
.146	.470	.131	.732	41.4 (6 hr.)	2.38
1.46	.441	.100	.641	39.9 (6 hr.)	2.27
1.46	.446	.108	.662	39.0 (6 hr.)	2.20
Solvent acetic anhydride, temperature 65°					
0.145	0.589	0.097	0.783	41.8 (6 hr.)	2.50
.145	.577	.106	.789	41.1 (6 hr.)	2.45
1.45	.500	.115	.730	44.8 (6 hr.)	2.75
1.45	.510	.115	.740	43.3 (6 hr.)	2.63
Solvent methyl ethyl ketone, temperature 65°					
0.145	0.648	0.089	0.826	55.0 (6 hr.)	3.52
.145	.652	.092	.836	54.5 (6 hr.)	3.44

TABLE IV (*Continued*)

Concn. peroxide × 10^2, M	C_2H_6/CO_2[a]	C_4H_{10}/CO_2	Total[a]/CO_2	% Decomp. (2 hr.)	kCO₂-- 10^6, sec.$^{-1}$
1.45	.636	.095	.826	19.8 (2 hr.)	3.10
1.45	.634	.101	.836	19.6 (2 hr.)	3.07
Solvent nitrobenzene, temperature 65°					
0.145	0.092	0.131	0.354	39.9 (5 hr.)	2.82
.145	.093	.133	.359	40.40 (5 hr.)	2.86
1.45	.110	.138	.386	39.3 (5 hr.)	2.77
1.45	.108	.142	.392	40.1 (5 hr.)	2.84
Solvent dioxane, temperature 65°					
0.156	0.676	0.100	0.876	39.7 (5 hr.)	2.81
.156	.672	.103	.878	40.0 (5 hr.)	2.83
1.56	.709	.126	.961	40.0 (5 hr.)	2.83
1.56	.719	.111	.941	39.5 (5 hr.)	2.79

[a] Total/CO_2 = (ethane + ethylene + 2butane)/CO_2. C_2H_6/CO_2 denotes (ethane + ethylene)/CO_2.

TABLE V

Solvent, isoöctane; temperature, 65°

Peroxide concn. × 10^2, M	Time, hr.	Scavenger	Mole % of scavenger	C_2H_6/CO_2[a]	C_4H_{10}/CO_2	$k_{CO_2} \times 10^{-5}$ sec.$^{-1}$
1.25	2	*p*-Benzoquinone	0.05	0.073	...	1.00
1.25	2	*p*-Benzoquinone	.05	.077	...	1.06
0.121	14	*p*-Benzoquinone	.1	.080	...	1.02
0.121	14	*p*-Benzoquinone	.1	.076	...	0.97
1.21	2	*p*-Benzoquinone	.5	.087	0.160	.95
1.21	2	*p*-Benzoquinone	.5	.080	.152	.97
1.45	2	*p*-Benzoquinone	Excess	.079	...	.90
1.45	2	Iodine	.3	.069	...	.95
1.45	2	Iodine	.3	.075	...	.92
1.45[b]	1.5	*p*-Benzoquinone	Excess	.074	...	12.7
1.45[b]	1	*p*-Benzoquinone	Excess	.078	..	12.3
				Av. 0.077 ± 0.004		

[a] C_2H_6 denotes C_2 hydrocarbons, *i.e.*, $C_2H_6 + C_2H_4$. [b] Experiments carried out at 85°.

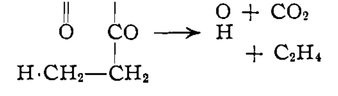
decomposition carried out at 85° in isoöctane solution, in spite of the fact that this rise in temperature increases the rate of decomposition by more than a factor of ten and, therefore, the stationary concentration of radicals by about a factor of ten. The same remarks apply to the results obtained in other solvents, showing that the described phenomenon is quite general. On the other hand, it is expected that the magnitude of the ratio C_4H_{10}/CO_2 should depend somehow on the nature of the solvent, and indeed small variations in this ratio are observed; the highest value of $C_4H_{10}CO_2$ is found in toluene solution (C_4H_{10}/CO_2 = 0.154), while the lowest is found in methyl ethyl ketone solution ($C_4H_{10}/CO_2 \approx 0.094$).

The reality of a cage reaction is confirmed further by a series of experiments in which an efficient radical scavenger was added to the solution of the peroxide. The results are shown in Table V. Small amounts of *p*-benzoquinone added to the solution of propionyl peroxide in isoöctane decreased considerably the amount of C_2 hydrocarbons formed (this is the consequence of the reaction C_2H_5 + *p*-quinone → non-gaseous addition product[12]). However, the ratio C_4H_{10}/CO_2, as well as the rate of decomposition were not affected by the presence of quinone. All these results parallel similar observations made previously during the investigation of the decomposition of acetyl peroxide.[13]

If *all* the C_2 hydrocarbons formed in the decomposition of propionyl peroxide result from the reaction

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

then by adding a sufficient amount of an efficient scavenger to the solution of the peroxide one should reduce the C_2H_6/CO_2 ratio to zero. However, inspection of Table V shows that a small but constant amount of C_2 hydrocarbons is formed even in the presence of a considerable amount of an efficient scavenger like quinone or iodine. The fact that the amount of these residual C_2 hydrocarbons is independent of the concentration of the scavanger (assuming that this concentration exceeds some limiting value) and independent of the nature of the scavenger, leads to the conclusion that the residual C_2 hydrocarbons are formed either in a "cage" disproportionation of ethyl radicals or by another mode of a unimolecular decomposition of the peroxide, *e.g.*



$$\begin{array}{l} C_2H_5{\cdot}\underset{\displaystyle O}{\underset{\|}{C}}{\cdot}O{\cdot}\underset{\displaystyle \underset{\displaystyle H{\cdot}CH_2\text{—}CH_2}{\underset{|}{CO}}}{\underset{|}{O}} \longrightarrow \begin{array}{l} C_2H_5{\cdot}C{:}O \\ \quad O + CO_2 \\ \quad H \\ \qquad + C_2H_4 \end{array} \end{array} \qquad (6)$$

The "cage" disproportionation leads to equal amounts of ethane and ethylene, while reaction (6)

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(12) The addition reactions are discussed in the following paper, THIS JOURNAL, **78**, 3322 (1956).

(13) A. Rembaum and M. Szwarc, *ibid.*, **77**, 3486 (1955).

forms ethylene and propionic acid. Consequently, determination of the C_2H_6/C_2H_4 ratio in the residual C_2 hydrocarbons is necessary for understanding the mechanism of their formation.

Determination of the amounts of ethylene present in the residual C_2 hydrocarbons was carried out by two techniques. Two samples were analyzed by means of a mass spectrometer by Dr. L. Friedman of Brookhaven National Laboratories, whom we thank here for his kind assistance, while the third one was analyzed by the hydrogenation procedure described by Shepp and Kutschke.[14] The following results were obtained

	C_2H_6/C_2H_4, dec. at 65°	C_2H_6/C_2H_4, dec. at 85°
Mass spectrometer	0.40	0.30
Hydrogenation	.36	..

We conclude, therefore, that at 65° and in isooctane solution about $^4/_7$ of the decomposition producing the residual C_2 hydrocarbons proceeds by the cage disproportionation, while the remaining ethylene is formed by reaction (6). This means that about 7% of the peroxide decomposes according to equation 6, while the decomposition of the remaining 93% results from reaction (1) and from the induced decomposition. We should expect, therefore, a loss of about 3.5% of CO_2 as a result of reaction (6), in addition to the loss resulting from the induced decomposition. Unfortunately, our experimental technique is not sufficiently refined to detect with certainty such small effects, and this is clear from the following data

Peroxide concn. × 10^3, *M*	1.21	14.5	82.0
$10^5 \times k$, from Fig. 1	0.99	1.14	1.45
$10^5 \times k_{CO_2}$ computed	.96	1.03	1.19
$10^5 \times k_{CO_2}$, obsd.	.88	1.03	1.18

k_{CO_2} computed is calculated as $k_I + 1/2(k_{exp} - k_1)$, on the assumption that reaction (1) and the induced decomposition are the *only* reactions consuming the peroxide.

More direct evidence in favor of reaction (6) would be given by an analysis of the liquid products of the decomposition for propionic acid. It is again unfortunate that we do not possess any analytical technique for determining small amounts of propionic acid in the presence of propionyl peroxide, since the hydrolysis of the latter interferes with titration. This difficulty was eventually overcome by analyzing the products resulting from complete decomposition of the peroxide (although such procedure leads to some ambiguities which are discussed in the last part of this paper), and thus the presence of 11% of the acid was demonstrated in the products.

It is instructive to contrast the behavior of acetyl peroxide and propionyl peroxide as far as the formation of acid is concerned. It was shown in previous studies[9] that not more than 1% of acid is formed by the complete decomposition of acetyl peroxide in isoöctane solution, and this result was checked and confirmed in the present investigation. It seems that the difference in behavior results from two factors. The transition state in reaction (6) can be attained for a greater number of configurations in the case of propionyl peroxide than in the case of acetyl peroxide, and, what is much more important, the formation of a double bond is possible only in the decomposition of propionyl peroxide, not in the decomposition of acetyl peroxide, and its formation adds to the driving force of reaction (6).

To ascertain that no ethylene is formed from free "floating" ethyl radicals, *i.e.*, from ethyl radicals which escaped from the "cage," the C_2 hydrocarbons formed by the decomposition of propionyl peroxide in iso-octane solution in *absence* of quinone were hydrogenated. The amount of ethylene detected was the same as that formed in presence of quinone.

It is interesting to compare the probabilities of cage disproportionation to cage recombination with the same ratio obtained in gaseous reaction of ethyl radicals. From our data (probability of disproportionation/probability of dimerization)$_{\text{in a "cage"}}$ = 0.044/0.3 = 1:7, the same ratio obtained from the study of gaseous decomposition is 1:9, *i.e.*, within experimental error the same results are obtained in both cases. This is satisfactory, since the probabilities for various modes of interaction of two ethyl radicals should be essentially independent of the surroundings.

Let us consider now the reactions responsible for the formation of ethane. The bulk of the ethane is formed by reaction (5)

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

and the solvent radicals S·, formed in this reaction, disappear mainly in a bimolecular process

$$S\cdot + S\cdot \longrightarrow \text{products} \qquad (7)$$

If reaction (7) consumes *all* the solvent radicals, the ratio $(C_2H_6 + 2\ C_4H_{10})/CO_2$ = "total"/CO_2 should be unity,[15] while the experiments show that this value is substantially less than unity. It appears, therefore, that a fraction of ethyl radicals is lost, probably through reaction (8)

$$C_2H_5 + S\cdot \longrightarrow C_2H_5S \qquad (8)$$

As the stationary concentration of S· radicals increases, reaction (8) competes more successfully with reaction (5) for ethyl radicals. The increase of the stationary concentration of S· radicals may be achieved either by increasing the concentration of the peroxide or by raising the temperature of the decomposition. Since the activation energy of reaction (5) is small, while the activation energy of the decomposition exceeds 30 kcal./mole, the increase in the stationary concentration of S· radicals would exhibit approximately the same effect if either of these two methods is used to enhance the rate of decomposition by the same factor. This deduction is confirmed by the following data. At 65° and in 0.121×10^{-2} *M* solution of the peroxide in isoöctane, the ratio C_2H_6/CO_2 is 0.602 ± 0.004. An increase of the concentration of the peroxide by a factor of ten, at constant temperature, decreases the C_2H_6/CO_2 ratio to 0.561 ± 0.007, while the increase in the rate of decomposition by a factor of 14, resulting from the rise in temperature by 20°, leads to $C_2H_6/CO_2 = 0.552$.

A very low value of C_2H_6/CO_2 ratio, as well as

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[14] A. Shepp and A. O. Kutschke, *Can. J. Chem.*, **32**, 1112 (1954).

[15] The disproportionation products are included in the expression "C_2H_6," *i.e.*, "C_2H_6" means *all* the C_2 hydrocarbons produced by the decomposition.

"total"/CO_2 ratio, is observed for the decomposition proceeding in benzene or in nitrobenzene solution. This phenomenon is explained in terms of addition reactions, *e.g.*

$$C_2H_5\cdot + C_6H_6 \longrightarrow \cdot C_6H_6\cdot C_2H_5$$

Such addition reactions of methyl radicals to aromatic compounds like benzene were observed previously,[9,16] and the investigation described in the following paper confirms fully the verity of addition of ethyl radicals to various aromatic compounds.

Ethyl radicals probably also add to toluene, but simultaneously with the addition reaction, the hydrogen abstraction reaction

$$C_2H_5 + C_6H_5\cdot CH_3 \longrightarrow C_2H_6 + C_6H_5\cdot CH_2$$

takes place. Since toluene is an efficient transfer agent, a comparatively high ratio of C_2H_6/CO_2 is observed in the decomposition proceeding in toluene. On the whole, one would expect that the ratio C_2H_6/CO_2 would be particularly high for the decomposition proceeding in a solvent which is an efficient transfer agent. It is interesting to note, therefore, that the highest value of C_2H_6/CO_2, as well as "total"/CO_2, was observed in decompositions proceeding in methyl ethyl ketone solution and dioxane solution, and indeed studies of reactions involving methyl radicals[17] proved that the reaction $CH_3 + CH_3\cdot CO\cdot C_2H_5 \rightarrow CH_4 + S\cdot$ proceeds nine times faster than the reaction $CH_3 +$ isoöctane $\rightarrow CH_4 + S$.

Decomposition in Polar Solvents.—The decomposition of propionyl peroxide in polar solvents differs in some respects from the reaction proceeding in hydrocarbon solutions. The data collected in Table I show that the first-order rate constants, measured by the disappearance of the peroxide, are substantially higher for the reaction in polar solvents. Moreover, while the amount of CO_2 produced in hydrocarbon solvents is accounted for on the assumption that the homolytic rupture of the O—O bond and the induced decomposition are the *only* reactions consuming the peroxide (reaction (6) seems to account for few per cent. of decomposition only), the amount of CO_2 formed in polar solvents is substantially lower than the expected one, judging from the amount of peroxide decomposed.

It appears, therefore, that in addition to the homolytic rupture of the O–O bond, a new mode of decomposition is operative in polar solvents, and that the latter reaction either does not produce any CO_2, or that it produces less CO_2 than reaction (1), followed by the decarboxylation of propionate radicals.

Although we cannot suggest any satisfactory mechanism for this additional mode of decomposition, we feel that the discussion of a few plausible mechanisms would be instructive and desirable. It is generally accepted that polar solvents enhance reactions involving polarized or ionized transition states. Thus, it would be natural to suppose that a transient separation of charges takes place in the transition state of the reaction discussed here, *e.g.*, $R\cdot CO\cdot\overset{+}{O}\cdot\overset{-}{O}\cdot CO\cdot R$, and that the heterolytic decomposition, favored by polar solvents, proceeds simultaneously with homolytic decomposition. Such a mode of decomposition has been considered by Leffler,[18] who investigated the decomposition of *p*-nitro-, *p*-methoxybenzoyl peroxide. In this compound the polarization of the O–O bond is favored by the opposing electronegativities of the nitro and the methoxy groups, while the symmetrical structure of propionyl peroxide makes such a polarization less probable. The subsequent steps following the polarization require either a donation of a proton from an acidic solvent, *i.e.*

$$\begin{array}{c} R\cdot CO\cdot\overset{+}{O}\cdot\overset{-}{O}\cdot CO\cdot R + HS \longrightarrow R\cdot CO\cdot\overset{+}{O},\ \overset{-}{S} + RCOOH \\ \downarrow \\ R\cdot CO\cdot OS \end{array}$$

or a rearrangement of the molecule, *e.g.*

$$R\cdot CO\cdot\overset{+}{O}\cdot\overset{-}{O}\cdot CO\cdot R \longrightarrow R\cdot O\cdot CO\cdot O\cdot CO\cdot R\cdot$$

Both reactions would lead to the disappearance of the peroxide without producing CO_2 or C_2 hydrocarbons and, indeed, an investigation of the products resulting from a complete decomposition of propionyl peroxide in dioxane solution demonstrated the presence of an acid and of an ester.

One might expect a polarized molecule to react easily with acids, and thus in acetic acid solution the following processes would be anticipated

$$CH_3COOH + C_2H_5\cdot CO\cdot\overset{+}{O}\cdot\overset{-}{O}\cdot CO\cdot C_2H_5 \longrightarrow CH_3\cdot CO\cdot O\cdot O\cdot CO\cdot C_2H_5 + C_2H\cdot COOH\cdot$$

The ultimate formation of methane should[5] be a natural consequence of such a reaction. However, no methane was found amongst the products of decomposition proceeding in acetic acid solution. This result parallels the previous observation,[9] namely, that the decomposition of acetyl peroxide in propionic acid solution does not produce any additional amount of ethane.

An acid-catalyzed decomposition of peroxides has been postulated by Bartlett and Leffler,[19] who studied the decomposition of phenylacetyl peroxide. The first-order rate constant of this decomposition was claimed to increase with the square root of initial concentration of the peroxide, *i.e.*, although any individual run obeyed the first-order kinetics, the derived first-order rate constant was proportional to the square root of initial concentration. The phenomenon was explained by Bartlett and Leffler in terms of acid catalysis, the acid–phenylacetic acid being formed as a product of the reaction. There is, however, an inconsistency in this explanation, since the proposed mechanism would lead to an autocatalytic reaction and not to a first-order decomposition. This remark does not invalidate, however, the hypothesis of acid catalysis which was verified by adding various amounts of acids to the solution of the peroxide.

Finally, let us consider the possibility of reaction (6) being the reaction which is enhanced by polar solvents. It is reasonable to consider reaction (6)

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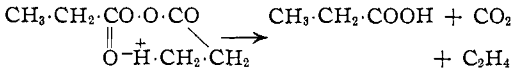
[16] M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954); THIS JOURNAL, **77**, 1949 (1955).

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

[18] J. E. Leffler, *ibid.*, **72**, 67 (1950).

[19] P. D. Bartlett and J. E. Leffler, *ibid.*, **72**, 3030 (1950).

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



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

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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Ethyl Affinities of Aromatic and Olefinic Compounds

BY J. SMID AND M. SZWARC

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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.