group is known[10] to have the greatest electron affinity, here again it would appear that this drain of electrons from the metal ion does contribute to the over-all stability of these complexes.

(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 188.

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Remarks on a Cage Reaction*

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RECEIVED FEBRUARY 14, 1955

Frank and Rabinowitch[1] were the first to point out that molecules (or fragments) undergoing a bimolecular collision in a liquid medium are confined to a cage formed by the solvent molecules. This "cage effect" is responsible also for the recombination of fragments produced in a unimolecular dissociation process, and such a reaction should be distinguished from the ordinary bimolecular recombination. While the latter reaction takes place between "free" fragments which lost their identity, the cage recombination involves the two original fragments produced by the dissociation of a single molecule.

The cage recombination of acetate radicals has been investigated recently and the results are discussed in this note. Acetate radicals are produced by the unimolecular decomposition of acetyl peroxide (reaction 1)

$$(CH_3{\cdot}COO)_2 \longrightarrow 2CH_3{\cdot}CO_2 \qquad (1)$$

The decomposition of a dilute solution of this compound in isoöctane yields the following products only: methane, ethane, carbon dioxide and the products of disproportionation of isoöctyl radicals. The first and the last products result from reactions 2 and 3

$$CH_3{\cdot} + \text{iso-}C_8H_{18} \longrightarrow CH_4 + \text{iso-}C_8H_{17} \qquad (2)$$

$$2\text{iso-}C_8H_{17}{\cdot} \longrightarrow \text{disproportionation products} \qquad (3)$$

while the formation of ethane has been attributed[2] to a cage recombination of acetate radicals. Let us repeat briefly the facts which led to this conclusion.

The fraction of methyl radicals which appears as ethane is given by $2C_2H_6/CO_2$. Now, the latter ratio is 0.169 ± 0.014 (an average of 8 experiments) at 65°, but only 0.094 ± 0.018 (an average of 7 experiments) at 85°. These results were obtained by decomposing an approximately $5{\cdot}10^{-3}$ M solution of acetyl peroxide in isoöctane. The stationary concentration of radicals at 85° is, however, about 10 times higher than at 65°, since the rate of decomposition increases by a power of ten over this temperature range. Hence, the above results definitely exclude a bimolecular recombination of "free" methyl (or acetate) radicals as a source of ethane. On the other hand, the observed decrease in $2C_2H_6/CO_2$ with increasing temperature would be expected if the ethane results from a cage recombination, since the probability of a radical escaping from the cage increases with rising temperature.

Further evidence in favor of a cage reaction is provided by experiments carried out in the presence of quinone. Table I shows clearly that increasing the concentration of quinone in the solution decreases considerably the ratio CH_4/CO_2, leaving $2C_2H_6/CO_2$ essentially unchanged. Since the presence of quinone does not affect the rate of the unimolecular decomposition (measured by the rate of formation of CO_2), it is obvious that quinone reacts with "free" radicals, and that the ethane does not result from the recombination of such radicals. Similar results were obtained in isoöctane solution using iodine as a scavenger (see Table II).

TABLE I

$(Ac_2O_2) = 2.5.10^{-2}$ M in toluene soln., $T = 65°$.

Concn. quinone in toluene	C_2H_6/CO_2	CH_4/CO_2	Concn. quinone in toluene	C_2H_6/CO_2	CH_4/CO_2
None	0.12 (av. value)	0.74 (av.)	0.05	0.08	0.37
0.025	.12	.54	.1	.09	.25
.050	.13	.37	.2	.09	.14
.05	.15	.35	.2[a]	.08	.08

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

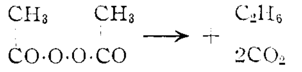
TABLE II

DECOMPOSITION OF DIACETYL PEROXIDE IN THE PRESENCE OF IODINE LIQUID PHASE

Acetyl peroxide in isoöctane $C = 5{\cdot}10^{-3}M$; $T = 85°$; decomp. ~ 60%.

Mole % of I_2	$2C_2H_6/CO_2$	CH_4/CO_2	$k \times 10^5$, sec.$^{-1}$
0.0	0.072	0.80	1.31
.1	.062	.010	1.25
.2	.062	.001	1.33

However, before one reaches the final conclusion that ethane *is* definitely formed in a cage reaction, one has to consider the possibility of two unimolecular modes of decomposition of acetyl peroxide which proceed simultaneously. One reaction (equation 1) leads to the rupture of the O–O bond and to the formation of radicals, while the second (equation 4) results from the C–CH_3 bond bending vibrations and yields ethane and two molecules of carbon dioxide in one step.



$$\begin{matrix} CH_3 & CH_3 \\ \vdots & \vdots \\ CO{\cdot}O & O{\cdot}CO \end{matrix} \longrightarrow \begin{matrix} C_2H_6 \\ + \\ 2CO_2 \end{matrix} \qquad (4)$$

If reaction 4 indeed takes place, its products should be observed in the liquid phase decomposition as well as in the gaseous decomposition. On the other hand, the products of the cage recombination cannot be observed in the gaseous decomposition, since this reaction is restricted to the liquid phase only. However, ethane is the main product of the gaseous decomposition, this product being formed by the recombination of methyl radicals.[3] Hence, in order to discriminate between these two alternatives: a cage reaction and reaction 4, we have carried out a series of experiments in which iodine vapor was

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* This investigation was supported by a grant from the National Science Foundation.

[1] N. H. Frank and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[2] M. Levy and M. Szwarc, THIS JOURNAL, **76**, 5981 (1954).

[3] A. Rembaum and M. Szwarc, *ibid.*, **76**, 5975 (1954).

mixed with acetyl peroxide, the gaseous mixture decomposed, and the products analyzed. The results are summarized in Table III. It can be seen that the iodine does not react with acetyl peroxide (the rate constant for the unimolecular decomposition is unaffected by the presence of iodine vapor). However, iodine reacts efficiently with methyl radicals, and consequently the ratio $2C_2H_6/CO_2$ is reduced effectively to zero as the partial pressure of iodine vapor is raised to 0.23 mm. These results prove conclusively that reaction 4 does not take place and, therefore, we conclude finally that the formation of ethane in the liquid phase decomposition must be attributed to a cage reaction.

TABLE III

DECOMPOSITION OF DIACETYL PEROXIDE IN THE PRESENCE OF IODINE VAPOR

Gaseous phase, $T = 461°K.$; flow system; partial pressure of peroxide about 0.1 mm.; partial pressure of the carrier gas (toluene) about 15 mm.

Partial pressure of I_2, mm.	$2C_2H_6/CO_2$	k, sec.$^{-1}$
0.00	1.00	1.95
.064	0.034	1.74
.12	.020	1.69
.23	.0004	1.80

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The Thermal Decomposition of Triazobenzene in Solution

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RECEIVED MARCH 10, 1955

The thermal decomposition of azo compounds such as 2,2′-azo-bis-isobutyronitrile in solution involves the splitting out of nitrogen and the production of two monoradicals. It would be expected that triazobenzene would decompose to give a diradical and nitrogen.

$$PhN_3 \longrightarrow PhN< + N_2$$

Evidence for such a mechanism comes from studies of the products of decomposition of triazobenzene in benzene and *p*-xylene.[1] Bertho showed that azobenzene and aniline were formed, the azobenzene probably arising from combination of two diradicals and the aniline from hydrogen abstraction reactions with the solvent. A kinetic study of the decomposition in solution has now been made to obtain support for such a mechanism and to establish the kinetic constants for the reaction. In addition an attempt has been made to use triazobenzene as a diradical source in the polymerization of methyl methacrylate.

Experimental

Triazobenzene was prepared from phenylhydrazine by the method of "Organic Syntheses."[2] It was twice distilled at reduced pressure in an atmosphere of nitrogen to give a pale yellow product. It was stored at 0°.

Tetrahydronaphthalene was distilled twice at reduced pressure in an atmosphere of nitrogen, and stored under dry nitrogen at 0°.

Nitrobenzene was subjected to crystallization and distilled at reduced pressure.

Methyl methacrylate (Rohm and Haas Company) was freed from inhibitor with sodium hydroxide solution, washed and dried, and distilled at 100 mm. pressure in an atmosphere of nitrogen. It was transferred to a vacuum apparatus and degassed four times and distilled twice *in vacuo*. It was stored at −80°.

Procedure.—Solutions of triazobenzene in the solvent, tetrahydronaphthalene or nitrobenzene, were made up over a wide concentration range. Five ml. of solution was placed in the apparatus consisting of a reservoir of volume 15 ml. attached to a capillary mercury manometer. The solution was thoroughly degassed and the apparatus sealed off. The reaction was followed by the pressure increase due to evolution of nitrogen; about 0.95 mole nitrogen was evolved per mole of triazobenzene decomposed. No correction for gas evolution from the solvent was necessary. Measurements were made over the temperature range 105–145°, the thermostat being controlled to ±0.1°. The manometer was heated to 5° above the temperature of the reservoir; under this condition the vapor phase reaction was negligible compared with the reaction in solution. Initial rates of reaction were used to determine the order of reaction and the dependence of rate on temperature. In two reactions which were followed to completion, a first-order law was accurately obeyed.

In experiments with methyl methacrylate, sealed tubes were used, and these were cooled and opened up to a manometer after definite time intervals to determine the amount of nitrogen formed. In parallel experiments the rate of polymerization of the methyl methacrylate was measured by precipitating the long chain polymer in methanol.

Results and Discussion

The rates of decomposition of triazobenzene in tetrahydronaphthalene and nitrobenzene were determined for the concentration range 0.0288–0.36 mole/l. triazobenzene at a temperature of 130°. The results are given in Table I. The rate of reaction is clearly proportional to the concentration of triazobenzene in both solvents. It is thus shown that the decomposition is a unimolecular process, almost certainly of the form

TABLE I

Concn. of triazobenzene, mole/l.	Rate in tetrahydronaphthalene $\times 10^6$, mole/l./sec.	Rate in nitrobenzene $\times 10^6$, mole/l./sec.
0.36	2.28	2.33
.144	0.936	0.950
.072	.482	.475
.0288	.210	.202

$$PhN_3 \longrightarrow PhN< + N_2$$

and does not involve a bimolecular process of the type

$$2PhN_3 \longrightarrow 2N_2 + PhN{=}NPh$$

nor an induced decomposition such as is observed with benzoyl peroxide.[3] Reaction rates were nearly the same for the two solvents, tetrahydronaphthalene and nitrobenzene, and it seems that the solvent does not take any part in the first step of the decomposition other than solvating the reactant to some extent.

The results for the dependence of first-order rate constant k on temperature are summarized in Table II. For tetrahydronaphthalene as solvent they can be expressed in the form

$$k = 2.51 \times 10^{12} e^{-32,500/RT}$$

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[1] A. Bertho, *Ber.*, **57B**, 1138 (1924).

[2] *Org. Syntheses*, **22**, 96 (1942).

[3] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).