TABLE I

PRODUCTS OF THE REACTION OF HOT HYDROGEN (RECOIL TRITIUM) ATOMS WITH cis AND trans DICHLOROETHYLENE

(Yields normalized to 10.0 for activity in hydrogen)

Starting material	Trans	Trans + O_2	Cis	Cis + O_2
Products				
Hydrogen	10.0	10.0	10.0	10.0
Ethylene	0.8	0.5	1.2	..
Acetylene	21.7	16.7	22.6	22.6
Methyl chloride	3.6	3.0	3.4	3.5
Vinyl chloride	77	51	72	52
Trans-Dichloroethylene	2.7	2.8	1.8	1.5
Cis-Dichloroethylene	1.3	1.4	3.9	3.1

excited to undergo cis-trans isomerization by internal rotation.

(B) Independent evidence also exists for a hot hydrogen addition reaction[11] similar to that for thermal atoms (see reaction 1). However, even for the hot system the resulting radical has been shown to have a strong preference to decompose by rupture of the weakest bond,[11] in this case to form vinyl chloride (see reaction 2). Nevertheless if de-excitation by C–H bond rupture occurs in only a few per cent. of the events, the addition mechanism could contribute significantly to the observed yield of the isomerized dichloroethylene.

Regardless of the relative importance of the isomerization mechanisms (A) and (B), the results demonstrate the existence of a fast hydrogen displacement reaction of hot hydrogen atoms with sp^2 C–H bonds. As with saturated systems this process probably proceeds by attack normal to the bond axis leading to a product of unchanged configuration. The "Impact Model" as the detailed mechanism of the fast displacement reaction is discussed in the two preceding papers.[6,7]

Studies of "Cage" Reactions

BY L. HERK, M. FELD AND M. SZWARC

The recombination of methyl radicals was investigated in the liquid and in the gaseous phases. The same temperature and the same proportion of ingredients were maintained in the respective experiments carried out in both phases. The occurrence of "cage" processes in solution was shown unequivocally. Two methods for methyl radicals generation were utilized in these studies, namely, thermal decomposition of acetyl peroxide and photolysis of azomethane. It was shown that "cage" recombination of acetate radicals leads to formation of methyl acetate since this product was not formed in the gaseous decomposition. By using the O^{18}-labeled peroxide it was demonstrated that the recombination of acetate radicals to the peroxide was not observed under our experimental conditions. From analysis of the results it was possible to estimate the unimolecular rate constant of acetate radical decarboxylation to be 10^9–10^{10} sec.$^{-1}$. It follows therefore that acetate radicals may participate in reactions taking place in the "cage," but the probability of their existence outside the "cage" is negligible. The "cage" recombination of methyl radicals, produced by the photolysis of azomethane, was investigated as a function of temperature and the wave length of actinic light. The close initial location of methyl radicals formed in this process increases greatly the probability of their recombination. Finally, the "cage" recombination of trifluoro-methyl radicals and the "cage" recombination and "cage" disproportionation of ethyl radicals is discussed. The results seem to indicate that the recombination of trifluoro-methyl radicals may require about 1.5 kcal./mole of activation energy. The large increase in the probability of recombination (or disproportionation) of ethyl radicals seems to be due to the larger size of the particle which decreases the probability of escape from the "cage" by decreasing the rate of diffusion.

The concept of "cage" reaction was introduced by Franck and Rabinowitch[1] to account for a peculiar situation created in solution when two radicals or free atoms are formed simultaneously in the same location. Due to the slowness of diffusion processes in liquids, the original partners remain together for about 10^{-10} sec., and this increases greatly the probability of their mutual interaction. This interaction is referred to by Franck and Rabinowitch as a "cage" reaction.

A more sophisticated treatment of "cage" processes is due to Noyes[2] who considered the problem of reunion of two particles starting their random walk through a liquid from adjacent locations and irreversibly reacting whenever they meet. This treatment led him to two concepts: (1) the probability of the initial "cage" reaction arising from an interaction of the original partners at the onset of their "walk," and (2) the prob-

ability of their reunion after being separated through diffusion.

Two types of events result from a "cage" reaction. Either the original partners recombine and regenerate the parent molecule, or they produce some new species. The first event contributes in a negative way to the outcome of a reaction. Its occurrence manifests itself only indirectly by slowing down the investigated decomposition process. This may be demonstrated by comparing the rates of a dissociation, proceeding under otherwise identical conditions, in the gas phase and in solution. If the reaction in solution is slower than its corresponding gaseous reaction, one might assume that the reduction in rate is caused by a "cage" process. Such phenomena are studied most conveniently in photo-dissociations where the occurrence of a "cage" reaction manifests itself by a decrease in quantum yield. Indeed, in the extreme case of reactions proceeding in rigid media at very low temperatures, "cage" processes may completely
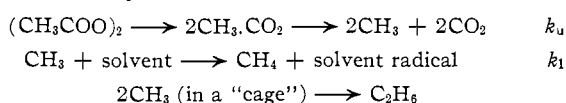
(1) J. Franck and E. Rabinowitch, Trans. Faraday Soc., 30, 120 (1934).

(2) R. M. Noyes, J. Chem. Phys., 18, 999 (1950), and the following papers.

arrest the photo-dissociation and reduce its quantum yield to zero.

Unfortunately, studies of such photo-dissociation processes are open to some criticism. One might suspect that other factors than "cage" reaction are responsible for the slowness or the inefficiency of the studied processes. For example, a photo-dissociation might require a transition of a molecule from its primary electronically excited state to a repulsive state. If this is the case, quenching of the excited species by the solvent may prevent its dissociation. Studies of the temperature dependence of the effect should be most helpful in resolving such a problem. The quenching process would be enhanced by raising the temperature, whereas the effect due to a "cage" reaction should be diminished (see e.g., the effect of temperature on the ethane yield in azomethane photolysis; the pertinent results are reported in the third part of this paper).

A "cage" reaction leading to formation of new species provides a much more satisfactory system for such a study. Here a "cage" reaction results in a positive effect, the absence of which can be demonstrated unambiguously by an experiment carried out in the gas phase. For example, decomposition of acetyl peroxide in solution produces ethane even at an extremely low concentration of the peroxide.[3] Addition of small amounts of scavengers, such as iodine or quinones, does not affect the rate of the decomposition, although it reduces substantially the amount of methane produced in the process.[3] These observations are accounted for by the mechanism

$$(CH_3COO)_2 \longrightarrow 2CH_3.CO_2 \longrightarrow 2CH_3 + 2CO_2 \qquad k_u$$

$$CH_3 + \text{solvent} \longrightarrow CH_4 + \text{solvent radical} \qquad k_1$$

$$2CH_3 \text{ (in a "cage")} \longrightarrow C_2H_6$$

Under the conditions of those experiments a truly bimolecular recombination of freely moving methyl radicals is negligible because their concentration is extremely low, whereas the concentration of the reactive solvent molecules is high. Hence, a methyl radical diffusing through the solvent has a much higher probability of reacting with it and forming methane than of recombining with another methyl radical.

Although the experiments involving scavengers are indicative, they are still not sufficient to prove conclusively the occurrence of a "cage" reaction. Formation of ethane might be attributed to a direct decomposition of a molecule of the peroxide in which a new CH_3—CH_3 bond is formed simultaneously with the fission of the existing CH_3–COO bonds. That this is not the case was proved by Rembaum and Szwarc[4] who investigated the gaseous decomposition of acetyl peroxide in the presence of iodine and showed the complete absence of ethane among the products of the reaction. However, a closer examination of their results casts some doubt on their conclusion. Their experiments in the liquid phase were carried out at 85°, whereas the gaseous reaction was investigated in the region of 200°. It could be argued

(3) M. Levy and M. Szwarc, J. Am. Chem. Soc., 76, 5981 (1954).

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

that the unimolecular decomposition of acetyl peroxide into ethane and $2CO_2$ corresponds to a substantially lower activation energy than its alternative decomposition into radicals resulting from a fission of the O–O bond. Consequently, the contribution of the former reaction could have been appreciable at 85° when the process lasted for an hour or so but may have been insignificant at 200° in a flow experiment in which the time of contact was only 1 sec. To dispel these doubts the present work was undertaken. At the same time it was decided to expand the studies of "cage" reactions to other systems and processes.

"Cage" Reactions in the Acetyl Peroxide Systems.—It was previously pointed out that decomposition of acetyl peroxide in isoöctane or toluene solution produces ethane.[3,4] It also was reported[3] that decomposition in sufficiently dilute isoöctane solution at moderate temperatures yields 2 moles of carbon dioxide for each mole of decomposed peroxide and that the ratio $(CH_4 + 2C_2H_6)/CO_2$ is unity. In the light of additional evidence now available it becomes apparent that both these statements are only approximately true. For example, averaging the data pertaining

Table I

Decomposition of Acetyl Peroxide in Isoöctane at 65°

Peroxide molarity $\times 10^3$	Styrene, mole %	CH_4/CO_2	$2C_2H_6/CO_2$	$\dfrac{CH_4 + 2C_2H_6}{CO_2}$	$\dfrac{CO_2}{\Delta \text{ Peroxide}}$
12.2	0.00	0.823	0.056	0.879	2.16 ± 0.30^a
12.2	.00	.818	.055	.873	2.18 ± 0.30^a
12.2	.00	.821	.055	.876	2.18 ± 0.30^a
12.2	.07	.547	.057		2.16 ± 0.30^a
12.2	.07	.547	.052		2.16 ± 0.30^a
12.2	.07	.547	.055		2.14 ± 0.30^a
12.2	.71	.118	.054		2.14 ± 0.30^a
12.2	.71	.117	.054		2.14 ± 0.30^a
12.2	.71	.117	.057		2.14 ± 0.30^a
12.2	7.00	.016	.049		2.10 ± 0.30^a
12.2	7.00	.016	.056		2.10 ± 0.30^a
12.2	7.00	.016	.054		2.10 ± 0.30^a
7.0	0.00	.819	.062	0.881	1.91 ± 0.1
7.0	.00	.817	.061	.878	1.91 ± 0.1
7.0	.00	.819	.059	.879	1.91 ± 0.1
7.0	7.00	.019	.052		1.87 ± 0.1
7.0	7.00	.024	.055		1.86 ± 0.1
7.0	7.00	.020	.057		1.86 ± 0.1
1.31	0.00	.808	.059	0.867	1.80 ± 0.04
1.31	.00	.817	.052	0.869	1.76 ± 0.04
1.31	.07	.501	.062		1.82 ± 0.04
1.31	.07	.498	.054		1.82 ± 0.04
1.31	.07	.499	.054		1.82 ± 0.04
1.31	.71	.110	.054		1.76 ± 0.04
1.31	.71	.111	.055		1.80 ± 0.04
1.31	.71	.111	.054		1.82 ± 0.04
1.31	7.00	.015	.063		1.84 ± 0.04
1.31	7.00	.017	.068		1.84 ± 0.04
1.31	7.00	.015	.052		1.82 ± 0.04

^{a} In view of the low percentage of decomposition ($\sim 16\%$) in the experiments involving higher concentrations of peroxide, Δ peroxide is a small difference of relatively large titers. This increases substantially although uniformly the experimental error for the CO_2/Δ peroxide in the series of respective experiments without affecting their relative values.

TABLE II

DECOMPOSITION OF ACETYL PEROXIDE AT 65° IN THE GAS PHASE AND IN SOLUTION

Phase	Reaction vol. (ml.)	Toluene, mole × 10⁵	1,4-Cyclo-hexadiene, mole × 10⁵	Acetyl peroxide, mole × 10⁵	Iodine, mole × 10⁵	Peroxide diluent × 10³	$\frac{CH_4}{CO_2}$	$\frac{2C_2H_6}{CO_2}$	$\frac{CH_4+2C_2H_6}{CO_2}$	$\frac{CO_2}{\Delta\ Perox.}$	$\left(\frac{Methyl\ acetate}{\Delta\ Perox.}\right)$
	5000	1800	...	3.86	...	2.05	0.502	0.234	0.736	1.858	<0.005
	5000	1880	...	3.86	...	2.05	.496	.223	.719	1.844	<0.005
	1000	470	...	0.79	...	1.68	.519	.168	.687	1.984	
	1000	470	...	.79	...	1.68	.513	.177	.690	1.956	
Gas	1000	470	...	.77	16.0	1.65	.0026	.0044	.0070	1.760	
	1000	470	...	.77	16.0	1.65	.0135	.0031	.0166	1.809	
	1000	36.2	488	1.83	...	3.49	.949	.012	.961	...	
	1000	36.2	488	1.83	...	3.49	.948	.026	.974	...	
	1000	...	529	~1.13	...	~2.14	.969	.014	.984	...	
Liquid	10	9400	...	19.3	...	2.05	0.673	0.046	0.719	1.758	0.150
	10	9400	...	19.3	...	2.05	0.672	0.046	0.718	1.764	0.160

to 6 earlier experiments[3] in which a $9 \times 10^{-3}\ M$ solution of acetyl peroxide was decomposed at 64.9°, one finds the ratio $CO_2/(decomp.\ peroxide)$ = 1.89 and the ratio $(CH_4 + 2C_2H_6)/CO_2 = 0.94$. Unfortunately, the experimental uncertainties of these data are too large to decide whether the observed deviations from the theoretically expected values are actually significant. We repeated, therefore, the pertinent experiments using a more refined technique and showed that these deviations are indeed real.

The results of our experiments are given in Table I. They show that at $1.30 \times 10^{-3}\ M$ concentration of the peroxide the ratios $CO_2/(decomp.\ peroxide)$ = 1.81 ± 0.02, $(CH_4 + 2C_2H_6)/CO_2 = 0.87 ±$ 0.01, and $2C_2H_6/CO_2 = 0.06 ± 0.01$. There is little doubt, therefore, that under these experimental conditions about 20% of the decomposed peroxide dissociates into $CH_3COOCH_3 + CO_2$. In fact, the calculation based on the ratio $CO_2/$ (Δ Perox.) leads to a value of 19% for the fraction of the peroxide decomposed into methyl acetate, whereas the value of 23% is derived from the ratio $(CH_4 + 2C_2H_6)/CO_2$. Hence, the decomposition of acetyl peroxide into methyl acetate is about 3.5 times as frequent as its decomposition into ethane. This is confirmed by direct determination of methyl acetate as reported in a later part of this paper.

The data collected in Table I show that addition of increasing amounts of styrene to the peroxide solution does not affect the ratios $CO_2/(decomp.\ peroxide)$ and $2(C_2H_6)/CO_2$, although it decreases greatly the yield of methane. These experiments confirm fully the previous findings[3,4] when iodine and quinone were used as radical scavengers.

The fact that the ratio $CO_2/(decomp.\ peroxide)$ is not affected by the presence of styrene deserves some further comment. In a recent paper Shine and Slagle[5] claimed that acetate radicals, formed by the pyrolysis of acetyl peroxide, add to cyclohexene and form the corresponding cyclohexyl acetate radicals. There is no reason to believe that the addition of acetate radicals to cyclohexene would be more favored than their addition to styrene. On the contrary, since methyl radicals add to styrene 800 times faster than to cyclohexene (unpublished data from this Laboratory), the re-

action of acetate radicals with styrene is expected to be faster than with cyclohexene. The fact that the latter reaction is not observed argues against Shine's suggestion. Actually, studies by Martin,[6] who investigated the decomposition of acetyl peroxide labeled by O^{18} in cyclohexene, imply that the ester may result from a specific reaction between the peroxide and cyclohexene. This conclusion, however, needs further verification.

To determine the nature of the reactions that yield ethane and methyl acetate, the decomposition of acetyl peroxide was reinvestigated in the gaseous phase at 65°. The pertinent experiments were performed in a static system, using large flasks as the reaction vessels. Toluene or cyclohexadiene-1,4 solutions of acetyl peroxide, or acetyl peroxide-iodine mixtures, were admitted into those flasks and then heated at the desired temperature for about 7 days to complete decomposition. The gaseous products were analyzed by the technique used in the solution experiments and in addition the absence of methyl acetate in the products was established by means of infrared spectroscopy. On the other hand, the same infrared test showed methyl acetate to be present in the products obtained in two experiments carried out to completion in the liquid phase at 65° in toluene solution. The determination of acetate was based on the intensities of the carbonyl and O–CH₃ stretching bands at 1740 and 1235 cm.⁻¹, respectively. A good agreement between the relative intensities of these two peaks proves that the product is indeed methyl acetate and not an acetate resulting from solvent radicals. Table II summarizes the pertinent results obtained in gaseous decomposition, as well as those derived from the two experiments carried out in solution.

The results obtained in gaseous decomposition in the presence of iodine vapor ($P_{I_2} = 3$ mm.) show that a negligible amount of ethane is formed at 65°, thus confirming the previous results obtained at 190°.[4] In fact, the amount of ethane generated in these experiments was less than 10% of that observed in similar experiments carried out in the liquid phase. Hence, at least 90%, and probably more, of the ethane formed in the liquid phase results from a "cage" recombination and not from a direct decomposition of the peroxide

(5) H. J. Shine and J. R. Slagle, J. Am. Chem. Soc., 81, 6309 (1959).

(6) J. C. Martin and E. H. Dew, ibid., 83, 1234 (1961).

molecule into CO_2 and C_2H_6. On the other hand, in the absence of iodine the fraction of methyl radicals undergoing recombination into ethane is higher in the gas phase (diluent toluene) than in the liquid phase, in spite of the fact that the ratio of the peroxide to diluent is the same in both types of experiments (see column 7 of Table II). Since most of the methyl radicals disappear from the system through their reaction with the diluent, their approximate stationary concentration is given by the equation

$$[CH_3] = \frac{2k_u[\text{Peroxide}]}{k_1[\text{Toluene}]}$$

where k_u and k_1 denote the rate constants of the unimolecular decomposition of the peroxide and of the bimolecular reaction 1

$$CH_3\cdot + C_6H_5\cdot CH_3 \longrightarrow CH_4 + C_6H_5\cdot CH_2 \qquad (1)$$

The rate of the unimolecular decomposition is only slightly higher in the gas phase ($k_u = 22.4\cdot10^{-5}$ sec.$^{-1}$ at 85°) than in toluene solution[7] (at 85° $k_u = 15.9\cdot10^{-5}$ sec.$^{-1}$). Hence, if the behavior of a liquid resembles that of a highly compressed gas, then for a constant peroxide/toluene ratio the stationary concentration of methyl radicals should be approximately the same in both phases. The rate of bimolecular recombination of methyl radicals would remain, therefore, the same in the gas phase and in solution,[7a] but the rate of their interaction with toluene is decreased in the gas phase because of low toluene concentration. Hence, the proportion of ethane in the products is inherently greater in experiments carried out in the gas phase than in solution.

The experiments carried out in 1,4-cyclohexadiene vapor show a considerable drop in the amount of ethane formed (see Table II). It was demonstrated[8] that H abstraction from this hydrocarbon is substantially faster than from toluene. In fact the ratio of the respective rate constants is estimated to be ~30. Therefore, the stationary concentration of methyl radicals must be substantially lower in 1,4-cyclohexadiene than in toluene and this reduces their recombination.

The data listed in the last column of Table II show that methyl acetate results entirely from a "cage" reaction and not from a direct decomposition of the peroxide into $CO_2 + CH_3COOCH_3$. It is necessary to stress that freshly prepared samples of acetyl peroxide were used in these experiments since the material stored in solution undergoes slow decomposition and this leads to accumulation of methyl acetate in older samples. It is gratifying to find that in the last two experiments given in Table II carbon dioxide and methyl acetate account for nearly all the CO_2 moieties of the decomposed peroxide, i.e. ($CO_2+CH_3CO-OCH_3$)/Δ Perox. is 1.9 and 1.93, respectively. On the other hand, the balance of products involving methyl fragments is less satisfactory. The interaction of toluene with methyl radicals involves not only H abstraction but also the addition; however,

(7) M. Levy, M. Steinberg and M. Szwarc, J. Am. Chem. Soc., 76, 5978 (1954).

(7a) This implies that the liquid behaves as a highly compressed gas.

(8) A. Rajbenbach and M. Szwarc, Proc. Chem. Soc., 347 (1958).

the product of addition has not been considered in our balance and its contribution may amount to about 20% of the formed methane. Correction for the addition products gives a more satisfactory balance, i.e., ($CH_4 + 2C_2H_6 + 2CH_3COOCH_3 +$ addition products)/(Δ Perox.) = 1.82. This value is still by 9% lower than the theoretical value of 2, although the reason for this deficiency is not clear. We suspect that it results from a slight error in the determination of methyl acetate.

The absence of any detectable amounts of methyl acetate in the gaseous decomposition is significant. Since bimolecular recombinations of radicals are favored under these conditions, our observations provide additional evidence for the rapidity of acetate radical decarboxylation.

"Cage" Reaction in Azomethane Photolysis.— The photo-decomposition of azomethane proceeds according to the equation

$$CH_3\cdot N{:}N\cdot CH_3 + h\nu \longrightarrow N_2 + 2CH_3\cdot$$
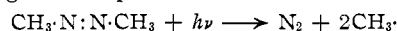
In our studies, isoöctane solutions of azomethane were photolyzed by means of a high pressure mercury lamp (General Electric AH-6) which radiates mainly in the 3600 Å. region and produces no light at wave lengths shorter than 3400 Å. It was demonstrated that for concentration of azomethane lower than 10^{-2} M methane, ethane and nitrogen were the only products of the decomposition. The product balance is given in Table III and

TABLE III

PHOTOLYSIS OF AZOMETHANE CARRIED OUT TO COMPLETION IN ISOÖCTANE SOLUTION[a]

T, °C.	Concn. of azomethane, moles/l.	CH_4/N_2	C_2H_6/N_2	($CH_4 + 2C_2H_6$)/N_2
~52	1.8×10^{-3}	0.576	0.722	2.02
~52	1.8×10^{-3}	.558	.708	1.97
~100	1.7×10^{-3}	.72	.66	2.04

[a] Composition of the mixture determined mass-spectrometrically. Rate of CH_3 formation less than 6×10^{-8} moles/cc. sec.

shows that the ratio ($CH_4 + 2C_2H_6$)/N_2 = 2. This fact suggests that ethane is not produced by a kinetically bimolecular recombination, but it must result from a "cage" reaction since no recombination of methyl radicals with solvent radicals is observed under these conditions. The latter reaction, if it occurs, should reduce the ($CH_4 + 2C_2H_6$)/N_2 ratio below its observed value of 2. A still more convincing evidence for "cage" reaction is presented by the data given in Table IV. These show that a hundred-fold variation of azomethane concentration has no effect on the proportion of the formed methane.

TABLE IV

PHOTOLYSIS OF AZOMETHANE IN ISOÖCTANE SOLUTION AT 50°

Concn. of azomethane, moles/l.	CH_4/N_2[a]
2.1×10^{-4}	0.535; 0.540
2.1×10^{-3}	.534; .540
2.1×10^{-2}	.523; .525[b]

[a] Each experiment was duplicated. [b] The slight decrease in the CH_4/N_2 ratio at 2.1×10^{-2} M concentration might indicate some bimolecular recombination of CH_3 and solvent radicals.

Phase	Reaction vol. (ml.)	Azomethane, mole $\times$ 10^5	1,4-Cyclo-hexadiene, mole $\times$ 10^5	$\dfrac{\text{Azo.}}{\text{Cyclo}} \times 10^3$	$\dfrac{CH_4}{N_2}$	$\dfrac{2C_2H_6}{N_2}$	$\dfrac{CH_4 + 2C_2H_6}{N_2}$	$\dfrac{N_2}{\Delta \text{ Azo.}}$
Gas	460	0.642	954	0.673	1.777	0.035	1.810[a]	1.03
Gas	445	0.579	954	.607	1.851	0.030	1.880[a]	1.09
Liquid	10	4.98	10600	.470	0.593	1.289	1.881[a]	0.89
Liquid	10	4.88	10600	.460	0.594	1.296	1.890[a]	0.90

[a] The failure of these values to approach 2.00 is due to addition of CH_3 to the molecules of the diluent. Assuming that the rate constant of methyl radical addition to a $C=C$ bond of cyclohexadiene-1,4 is the same as that found for *cis*-butene-2 and that the rate constant of hydrogen abstraction from the CH_2 groups of cyclohexadiene-1,4 is the same as that found for pentadiene-1,4, one calculates the ratio of rate of addition and the rate of abstraction to be $2 \times 3.4/4 \times 20 = 0.085$ (see Buckley and Szwarc, *Proc. Roy. Soc. (London)*, **A240**, 396 (1957), and Rajbenbach and Szwarc, *ibid.*, **A251**, 1266 (1959), for the pertinent data). This means that $(CH_3$ "lost" through addition)$/N_2$ should be approximately 0.05 in the liquid phase experiments and 0.15 in the gas phase experiments. These values are consistent with our observations.

In order to prove that ethane is not formed by a direct photodecomposition of azomethane molecule into ethane and nitrogen, the photolysis was reinvestigated in the gas phase. The pertinent experiments were performed simultaneously in the gas phase and liquid phase at the same temperature and at approximately the same molar ratio of azomethane to a hydrocarbon diluent. Cyclohexadiene-1,4 was chosen as a diluent because of its low boiling point, the presence of four extremely reactive methylenic hydrogens in its molecule, and the very low reactivity of its $C=C$ double bonds toward methyl radicals addition. Indeed, as demonstrated by the data shown in Table II, the addition of CH_3 radicals to that hydrocarbon may be neglected because of the much faster hydrogen abstraction reaction.

The results of photolysis carried out in gaseous and liquid cyclohexadiene-1,4 are given in Table V. A 5×10^{-3} M solution of azomethane in this solvent was either directly irradiated or first evaporated into $1/2$ liter cylindrical ampoules (the total pressure being about 500 mm.) and then irradiated in the vapor phase. The photolysis was carried out to completion and the products were analyzed by means of a mass-spectrometer. (Further details of experimental technique may be found in L. Herk, Ph.D. thesis, Syracuse, 1961.) It was most gratifying to find that negligible amounts of ethane (less than 1%) were formed in the gas phase, although in the liquid phase ethane constituted 65% of the products. Obviously, under these conditions a bimolecular recombination of methyl radicals has been eliminated even in the gas phase. The results demonstrate that azomethane does not decompose on photolysis into $C_2H_6 + N_2$ but into methyl radicals and N_2, reconfirming our conclusion that ethane in the liquid phase is formed by the "cage" reaction.[9]

The temperature dependence of a "cage" reaction is most conveniently studied in a photo-decomposition. For example, the photo-dissociation of azomethane permitted the investigation of the temperature dependence of methyl radicals "cage" recombination. A 3×10^{-3} M solution of azomethane in isoöctane was photolyzed to the extent of about 5% at temperatures ranging from 6 to 95°, and the ratio of CH_4/N_2 was determined in

(9) One may argue that the excited azomethane molecule is quenched by the solvent into a state leading to the decomposition into $C_2H_6 + N_2$. This, we believe, is not a plausible explanation.

each experiment. Assuming that the remaining methyl radicals combine quantitatively into ethane, one computes the ratio of the rate of diffusion of methyl radicals out of the "cage" to the rate of their recombination in the "cage" as equal to $(CH_4/N_2)/(2\text{-}CH_4/N_2)$. The experimental results are summarized in Table VI, and the plot of log $\{(CH_4/$

Table VI

Temperature Dependence of "Cage" Recombination of Methyl Radicals. Photolysis of Azomethane in Isoöctane Solution

At λ = 3600 Å.

T, °C.	Av. CH_4/N_2	$\dfrac{(CH_4/N_2)}{\{2\text{-}CH_4/N_2\}}$	No. of exp.
6	0.389 ± 0.004	0.242	4
25	$.454 \pm .006$	.293	4
50	$.543 \pm .009$	.372	4
75	$.674 \pm .006$	.506	9
95	$.766 \pm .009$	.623	7

At λ = 2537 Å.

T, °C.	CH_4/N_2	$\dfrac{(CH_4/N_2)}{\{2\text{-}CH_4/N_2\}}$	No. of exp.
0.2	0.274	0.159	1
0.2	.240	.136	1
21.5	.451	.291	1
21.5	.374	.230	1
25.1	.401	.251	1
25.1	.397	.248	1
45.0	.514	.346	1
45.0	.574	.403	1
69.9	.664	.497	1
69.9	.665	.498	1
74.9	.661	.494	1
74.9	.729	.574	1
95.7	.636	.466	1
95.7	.619	.448	1

$N_2)/(2\text{-}CH_4/N_2)\}$ *versus* reciprocal of absolute temperature, shown in Fig. 1, results in a good Arrhenius line corresponding to an activation energy of about 2 kcal./mole.

Similar experiments were carried out with a resonance mercury lamp using the 2537 Å. wave length as the actinic light. The results are included in Table VI and the respective Arrhenius plot is given also in Fig. 1. It is remarkable how closely the ratios of CH_4/N_2 obtained with 3600 and 2537 Å. light, respectively, are in agreement. This suggests that the excess of energy remains in the N_2 molecule and is not transferred into kinetic energy of methyl radicals since the rate constant of their reaction with solvent molecules apparently does

not increase with shorter wave length. Alternatively, the excited azomethane molecule may be quenched to the lowest excited state before it decomposes. Of course, the excess of kinetic energy, if any, is not expected to accelerate the escape of CH_3 radicals from the "cage," because the solvent molecules are so much heavier than the radicals. The activation energy for escape from the "cage" based on the results obtained with the resonance lamp seems to be slightly higher than that observed with the Hg high pressure lamp. The former is estimated to be about 3 kcal./mole, but the experimental uncertainty amounts to ±1 kcal./mole.

The activation energies for escape from the "cage" seem to be reasonable. On the assumption that "cage" recombination proceeds with zero activation energy, the activation energy of escape is expected to be of the same magnitude as that of the diffusion process. In fact, from the temperature dependence of isoöctane viscosity,[10] the corresponding activation energy of diffusion was calculated to be 2.1 kcal./mole.

Comparison of "Cage" Reactions and the Rate of Decarboxylation of Acetate Radicals.—The extent of "cage" recombinations of methyl radicals is greatly different in acetyl peroxide and azomethane systems. Although both reactions take place in the same solvent and at the same temperature, only 6% of recombination is observed in the first system, while about 65% of radicals recombine in the second. This great difference in the probability of methyl radicals recombination might be due to a different initial separation of the recombining species. In the decomposition of acetyl peroxide the radicals are separated by two, comparatively large, molecules of carbon dioxide, while only one, comparatively small, molecule of nitrogen separates them when azomethane is photolyzed.

Although this explanation is rational, we believe that the diminished probability of methyl radical recombination in the acetyl peroxide system results to a great extent from another factor. Photolysis of azomethane produces directly methyl radicals which may recombine in a "cage." On the other hand, pyrolysis of acetyl peroxide seems to yield as the primary products acetate radicals, and these in turn decarboxylate into methyl radicals and carbon dioxide.[14] Indeed, by establishing the fact that methyl acetate, found in the decomposition of acetyl peroxide, results from a "cage" recombination we furnish additional evidence for the *existence* of acetate radicals and for their formation in the course of acetyl peroxide decomposition. The "cage" recombination which produces methyl acetate may be due to reaction A or B. Unfortunately, we see no way for distinguishing between these two alternatives, although some indirect evidence seems to favor reaction B.

$$CH_3COO + CH_3 \longrightarrow CH_3 \cdot COO \cdot CH_3 \quad (A)$$

$$2CH_3 \cdot COO \longrightarrow CH_3 \cdot COO \cdot CH_3 + CO_2 \quad (B)$$

Having established the presence of acetate radicals in the "cage," it is reasonable to expect that some of these radicals may recombine and reform molecules of acetyl peroxide. In order to investi-
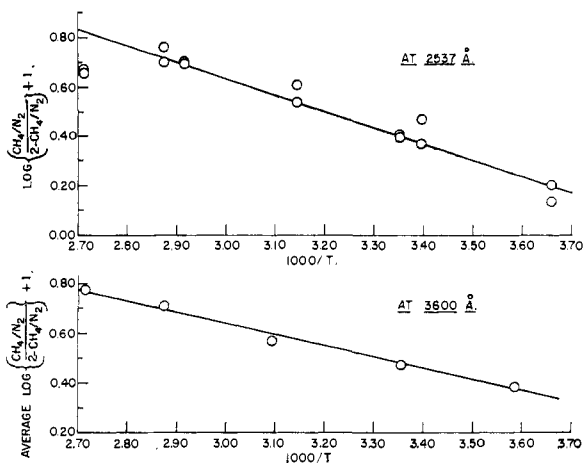
(10) A. H. Nisson, *Phil. Mag.*, **32**, 441 (1941).

Fig. 1.—Photodecomposition of azomethane in isoöctane.

gate this possibility acetyl peroxide labeled with O^{18} in its carbonyl group was prepared. The preparation followed the method described by Dr. Martin[6] and by using infrared analysis the percentage of extra labeling in the C=O group was determined to be 0.616 ± 0.007%. This result was checked by determining the total O^{18} content of the CO_2 formed by decomposition of the peroxide. The latter, determined mass-spectroscopically, was found to be 0.800 ± 0.006%. Correcting these results for naturally occurring O^{18} we find our labeling to be 100% effective.

If acetate radicals recombine to acetyl peroxide, we might expect scrambling of O^{18} in the reformed peroxide. However, after decomposing 55% of the labeled peroxide at 55° in pentane solution, we were able to show that the residual peroxide still contained 0.646 ± 0.030% of O^{18} in its C=O group. The sample was first crystallized from pentane, freed from methyl acetate formed in the reaction and then examined by infrared. It is concluded, therefore, that the recombination of acetate radicals into peroxide does not take place at all, presumably because such recombination forms methyl acetate through reaction B or that the "cage" recombination does not involve "scrambling." We are inclined to accept the first alternative in view of the discussion on "cage" disproportionation reported in the last part of this paper

Decomposition of acetyl peroxide in isoöctane solution is 30% slower than that observed in the gas phase.[7] In the past this decrease in the rate of decomposition was attributed tentatively to the "cage" recombination of acetate radicals into peroxide. In view of our present results we should attribute this difference to the general solvent effect.

The presence of acetate radicals in the "cage" must be contrasted with their absence outside the "cage." This absence is demonstrated, *e.g.*, by the negative results of Walling's experiments.[11] This worker tried unsuccessfully to trap acetate radicals using moist iodine as a scavenger. The same conclusion follows from the absence of ace-

(11) C. Walling, quoted in his monograph "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1958.

tic acid in the decomposition products.[3,12] Moreover, studies of Herk and Szwarc[13] showed that methyl, and not acetate, radicals abstract H atoms from ethylbenzene when acetyl peroxide is decomposed in this solvent. Since it is estimated that under these conditions the radicals react with the solvent molecules in about 10^{-7} to 10^{-8} sec., the average life time of acetate radicals must be substantially shorter than 10^{-8} sec., i.e., of the order 10^{-9} to 10^{-10} sec. Therefore, the unimolecular rate constant k_d of acetate radical decarboxylation seems to be 10^9 to 10^{10} sec.$^{-1}$ at 65°, corresponding to an activation energy of about 5 kcal./mole. This result confirms the conclusion drawn by Szwarc and Herk,[14] who discussed details of acetyl peroxide decomposition and deduced that the decarboxylation of acetate radicals must involve a small activation energy.

The high k_d value for the decarboxylation of acetate radicals is plausible in view of their lack of stability. The high exothermicity of their decarboxylation, estimated at 17 ± 5 kcal./mole,[15] supports this conclusion.

"Cage" Recombination of CF_3 Radicals.—Studies of photolysis of hexafluoroazomethane in isoöctane solution, carried out in this Laboratory, demonstrated that hexafluoroethane, trifluoromethane and nitrogen are the products of the reaction. At 65° the average ratios of CF_3H/N_2 and $2C_2F_6/N_2$ are 1.45 and 0.55, respectively, showing that the first two products account for all the CF_3 radicals formed in the photolysis. Addition of ethylene or isobutene reduces the ratio of CF_3H/N_2, without affecting the ratio of C_2F_6/N_2, and this suggests that C_2F_6 results from a "cage" recombination.

Assuming that C_2F_6 is formed by a "cage" recombination, it is interesting to compare the ratio C_2F_6/N_2 with C_2H_6/N_2 obtained in the photolysis of azomethane carried out at the same temperature and in the same solvent. The difference between these ratios is striking and demonstrates that the "cage" recombination of methyl radicals ($C_2H_6/N_2 = 1.4$) is much more efficient than that of trifluoromethyl radicals ($C_2F_6/N_2 = 0.55$). The decrease in the efficiency of CF_3 radicals recombination may be due to two factors. Since methyl radicals are much lighter than the solvent molecules (isoöctane), on collision with the latter their momentum is reversed and thus their imprisonment becomes more efficient. This effect might be reduced for CF_3 radicals. Their mass is approximately five times larger than that of CH_3 and consequently their escape from the "cage" should be facilitated.

Alternatively, one may assume that the recombination of polar CF_3 radicals involves a small activation energy while no activation energy, or at least a very small activation energy, governs the recombination of methyl radicals. If this is the case, the probability of CF_3 recombination should be lower than that of CH_3 recombination.

The temperature dependence of methyl radicals recombination was investigated by Gomer and Kistiakowsky[16] and found to be very small, corresponding to an activation energy of less than 0.7 kcal./mole. These results are essentially confirmed by later studies, e.g., those of Ingold and Lossing and of Ingold, Henderson and Lossing.[17] On the other hand, recent work of Pritchard and Dacey[18] indicates that the activation energy of CF_3 radical recombination might be as large as $1.5-2$ kcal./mole.

It is our intention to investigate to what extent the mass factor and the activation energy of recombination contribute to the decreased efficiency of "cage" recombination of CF_3 radicals. Assuming tentatively that the mass effect is small, i.e., that the rate of escape is approximately the same for both CH_3 and CF_3 radicals, we may equate the ratio of $(C_2F_6/CF_3H)/(C_2H_6/CH_4)$ to $\exp(-\Delta E/RT)$. Thus, a value of ~ 1.3 kcal./mole for ΔE is obtained in fair agreement with Pritchard and Dacey's findings.

"Cage" Recombination and "Cage" Disproportionation of Ethyl Radicals.—It was shown by Smid and Szwarc[19] that ethyl radicals produced by the thermal decomposition of propionyl peroxide undergo both "cage" recombination and "cage" disproportionation. Their data indicate that the same ratios for probabilities of recombination to disproportionation are observed in the "cage" process as in a gaseous bimolecular collision. This seems to indicate that no preferential orientation is preserved in the "cage." A similar conclusion may be drawn out from the results of recent studies of Hammond, et al.,[20] who investigated the bimolecular and "cage" recombination of $C(CH_3)_2 \cdot CN$ radicals.

A following point, emerging from the findings of Smid and Szwarc, needs some comment. While only 6% of the CH_3 radicals dimerize during the decomposition of acetyl peroxide approximately 35–40% of ethyl radicals combine or disproportionate in the course of pyrolysis of propionyl peroxide. It appears, therefore, that the probability of escape from the "cage" is much smaller for ethyl radicals than for methyl radicals. We believe that this effect shows the importance of particle size in determining the probability of "cage" reaction.

Although terms like "imprisonment" or escape from the "cage" were used throughout this paper, it should be emphasized that the processes investigated should not be described by the naïve concept of a "cage" formed by molecules of solvent. The more fundamental approach explored by Noyes is more realistic. The presence of solvent molecules changes the probability of finding the reacting partners further apart at a time t after their formation and therefore the probability of their recombination, during any time interval t,

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(20) S. Wu Chin-Hua, G. S. Hammond and J. M. Wright, ibid., 82, 5386 (1960).

is increased. The detailed models of the diffusion processes need further investigation. Nevertheless, for the sake of simplicity of expressions, the terms mentioned above may be used since they do not distort the real meaning of the investigated phenomena.

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Methyl Affinities of Some Cyclic Olefins and Polyenes

BY J. GRESSER, A. RAJBENBACH AND M. SZWARC

Methyl affinities of the following hydrocarbons were determined: cyclopentene, cyclohexene, cycloheptene, cyclooctene, norbornene, cyclopentadiene, 1,3-cyclohexadiene, bicyclo[2,2,1]heptadiene, cycloheptatriene, cyclooctatetraene, methylene-cyclobutane and 1,3-dimethylene-cyclobutane. The reactivities of all these compounds except cyclohexene conform to a logical pattern. The unexpectedly low reactivity of cyclohexene remains unexplained. Reactivity of 1,3-dimethylene-cyclobutane permits calculation of the β parameter in a "stretched" butadiene. It was found that $\beta_{2.11}/\beta_{1.39} = 0.124$. Some hydrogen abstraction reactions are discussed and the pertinent relative rate constants of hydrogen abstraction by methyl radicals are tabulated.

Pursuing our studies of methyl radical addition to olefinic compounds, we recently determined the rate constants of addition to a series of cyclic olefins, dienes and polyenes, with intention of investigating the effects of strain on the reactivity of these reagents. The investigated reactions were carried out in isoöctane solution at 65°. Methyl radicals were generated by a thermal decomposition of acetyl peroxide and the standard experimental technique, described, in a paper by Buckley and Szwarc,[1] was used in these studies. The results were obtained in the form of k_2/k_1, where the subscripts refer to reactions 2 and 1, respectively

$$CH_3 + \text{isoöctane} \longrightarrow CH_4 + \text{isoöctyl radical} \quad (1)$$

$$CH_3 + \text{olefin} \longrightarrow CH_3 \cdot \text{olefin} \quad (2)$$

Experimental Results

The experimental results obtained in the course of these studies are summarized in Table I which gives the relative rate constants of methyl radical addition (k_2/k_1) as well as the relative rate constants of α-hydrogen abstraction (k_3/k_1). The investigated cyclic monoölefins were obtained commercially and purified through distillation. Cyclopentadiene was prepared from the respective dimer, and after careful distillation the resulting product was immediately diluted with isoöctane and used for the determination of methyl affinity. Cyclohexadiene-1,3 was prepared by the method described in "Organic Synthesis," and after distillation it was also immediately diluted with isoöctane and then stored in the cold. Cyclohexadiene-1,4 and cyclooctatetraene were commercial products (Aldrich Chemical Co.) repurified before being used. Bicyclo[2,2,1]heptadiene and cycloheptatriene were kindly offered to us by Shell Development Co., and the values for respective k_2/k_1's were corrected in order to account for the presence of small amounts of impurities. Fortunately, these corrections are very small and therefore they cannot affect our basic conclusions. Norbornene was obtained from Dr. Winstein, whom we thank for this gift. Methylene-cyclobutane was obtained from Aldrich Chemicals and 1,3-dimethylene-cyclobutane was kindly provided by Dr. V. A. Engelhardt of the du Pont Co.

Discussion

The results quoted in Tabl I show that methyl affinities of cyclic mono-olefins are similar to those found for 2-butenes,[1] cyclohexene being, however, an exception. The methyl affinity (k_2/k_1) of the latter olefin is substantially lower than that of the remaining compounds. Apparently this observation is general and not restricted to the specific case of methyl radical addition. Indeed, Kharasch, et al.[2] found that the addition of CCl_3 radicals proceeds 3 times faster with cyclopentene than with cyclohexene.

The gradation of reactivities in the series of cyclic mono-olefins seems to be correlated with their heats of hydrogenation as shown in Fig. 1. Although this correlation is interesting, it remains to be seen whether it is meaningful. One usually expects that the rate of an exothermic reaction increases with increasing exothermicity. However, in the case of cyclic olefins, the *higher* exothermicity of hydrogenation is associated with the *slower* rate of addition. On the other hand, it should be kept in mind that the heat of hydrogenation is not equal to the heat of radical addition and, as a matter of fact, an increase in one entity need not necessarily be reflected by an increase in the other. The fact that the rate of addition to cyclohexene as well as the rate of H abstraction from this compound are both unusually low might indicate a very unfavorable strain in ⟨ S ⟩˙ and in ⟨ ⟩˙ radicals.

The reactivities of conjugated cyclic di-olefins show that 1,3-cyclohexadiene is more than twice as reactive as cyclopentadiene. This trend in the reactivity is confirmed by the change observed in the heats of hydrogenation. Both observations indicate a higher stability of cyclopentadiene than

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