

If so, reaction 8 should be retarded by pressure, while the addition of the dimer radical in (8) in another molecule of dichloroethylene would be facilitated, leading to the observed result.

We are currently investigating the effect of pressure on a variety of radical chain processes, and the results will be reported in due course.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

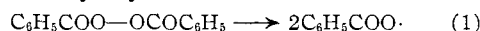
Organic Reactions under High Pressure. III. The Decomposition of Benzoyl Peroxide¹

BY CHEVES WALLING AND JOSEPH PELLON²

RECEIVED MARCH 25, 1957

The rate of decomposition of benzoyl peroxide in acetophenone solution at 80° is retarded 22% by a pressure of 1500 kg./cm.², corresponding to a value of $\Delta V^\ddagger = 4.8$ cc./mole for the unimolecular decomposition. At higher pressures a fast decomposition sets in which is apparently higher than first order and believed to represent a rapid induced radical chain reaction, although it is not affected by the presence of methyl methacrylate. At atmospheric pressure, the decomposition in cumene containing styrene is significantly accelerated by mercury.

In 1946, Bartlett and Nozaki³ and Cass⁴ proposed that the decomposition of benzoyl peroxide in organic solvents proceeds by both a spontaneous unimolecular decomposition and a subsequent induced chain, and this formulation is now generally accepted.⁵ The initial decomposition is apparently into two benzoyloxy radicals



which either lose CO₂ or attack reactive substrates in the decomposition medium. In aromatic solvents or other relatively inert media, the subsequent chain appears to involve attack on peroxide molecules by peroxide fragments,³ while in solvents such as ethers and alcohols (where the chain reaction is much more rapid) radicals derived from solvent act as chain carriers.^{4,6}

The analysis of the effect of pressure on organic free radical processes which we have developed in preceding papers⁷ suggests that reaction 1 should be slightly pressure retarded but that subsequent induced decompositions should be strongly accelerated since they involve chains of radical displacement or addition processes. In this paper we will see that, in acetophenone solution at 80°, both of these expectations are realized, although the nature of the induced chain has not been worked out. Acetophenone was chosen as a solvent since it has been studied in some detail by Blomquist and Buselli,⁸ and it is a medium in which there appears to be little induced decomposition at atmospheric pressure.

Experimental

Preliminary Experiments.—Since in our previous work on polymerization samples had been isolated from the pres-

(1) Taken from a portion of the dissertation of Joseph Pellon, submitted in partial fulfillment of the requirements for the Ph.D. degree, 1957. This work was also supported in part by the Office of Naval Research.

(2) Union Carbide and Carbon Corp. Fellow, 1955–1956.

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

(4) W. E. Cass, *ibid.*, **68**, 1976 (1946).

(5) For more extensive references than those given here, cf. A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

(6) P. D. Bartlett and K. Nozaki, *THIS JOURNAL*, **69**, 2299 (1947).

(7) C. Walling and J. Pellon, *ibid.*, **79**, 4776, 4782 (1947).

(8) A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).

sure-transmitting fluid by carrying out the reactions in glass vessels over mercury, we first undertook to see if mercury had any effect upon the rate of decomposition of relatively concentrated solutions of benzoyl peroxide. Decomposition rates of benzoyl peroxide were compared for samples in sealed degassed glass tubes and in similar tubes containing mercury. The solvent chosen for this preliminary work was cumene containing 0.2 molar styrene to eliminate any induced decomposition.⁹ With 0.01 *M* peroxide at 85°, identical first-order rates were observed, although peroxide titrations on the samples run in the presence of mercury were consistently 2–3% lower than the others. With 0.10 molar peroxide, the initial rate in the presence of mercury was approximately 17% faster than in its absence and the decomposition appeared somewhat autocatalytic. In addition, a heavy white precipitate of what was presumably an organomercury compound appeared in the tubes.¹⁰ For this reason the use of mercury as a sealing fluid was abandoned, and series of very inert, flexible vessels developed as shown in Fig. 1. For the work described here, the glass and Teflon (polytetrafluoroethylene) vessel A was employed, but subsequently design B¹¹ constructed of Teflon or Kel-F (polytrifluorochloroethylene) has been found more satisfactory. Such vessels have a capacity of 11 cc. and with a wall thickness of 0.014 in. will withstand several atmospheres internal pressure, so that low-boiling liquids can be introduced into the pressure system well above their boiling-points. Neither design showed detectable leakage on exposure to pressure cycles of 8000 kg./cm.² and can be used repeatedly without damage.

Technique of Pressure Experiments.—Solutions of benzoyl peroxide¹² were degassed and a slight excess transferred to the Teflon vessel with minimum exposure to air. The plug was inserted so that no gas bubble was left in the vessel, the top screwed on and the vessel and container placed in the pressure apparatus and brought to pressure as previously described. Comparison experiments at atmospheric pressure were run in sealed degassed glass tubes. At the end of a run peroxide was titrated by iodimetry essentially as described by Blomquist and Buselli.⁸

Results and Discussion

First-order plots of typical experiments are shown in Figs. 2 and 3. Considering first the experiments at 1500 kg./cm.² and below where first-

(9) C. G. Swain, W. T. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5429 (1950).

(10) The formation of phenylmercuric benzoate from the reaction of benzoyl peroxide with mercury in refluxing benzene has been described by G. A. Razuvaev, Y. A. Ol'dekop and L. N. Grobov, *Doklady Akad. Nauk S.S.S.R.*, **88**, 77 (1953); *Zhur. Obshchei Khim.*, **23**, 589 (1953).

(11) Designed by Mr. J. Peisach of this Laboratory.

(12) In general freshly distilled and carefully fractionated acetophenone was used as our solvent. However, no significant difference in rate was observed using commercial material as received.

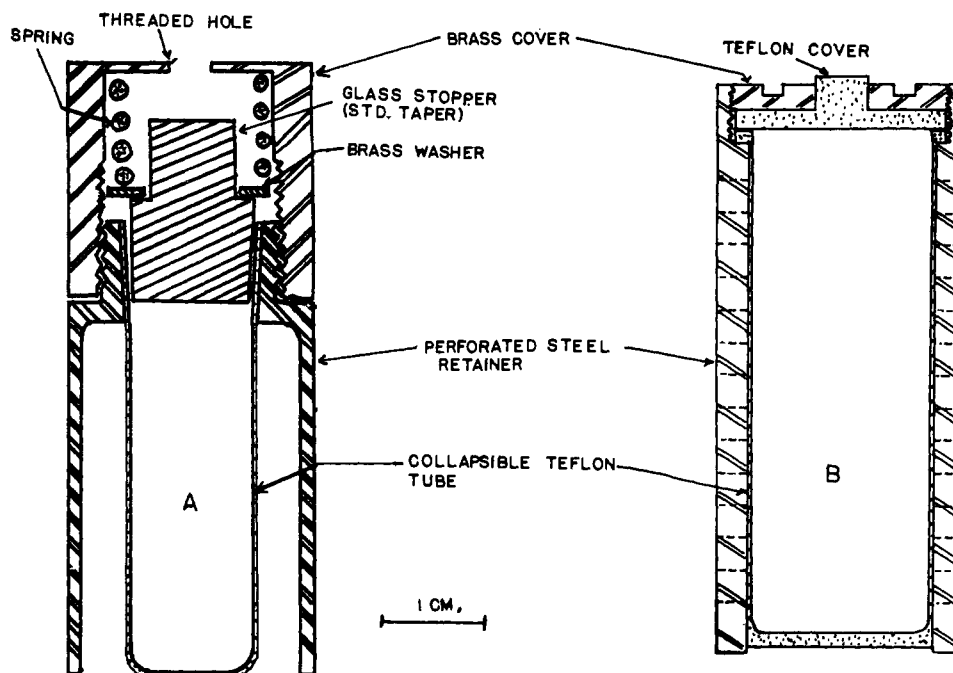


Fig. 1.—Internal reaction vessels for use in mercury sensitive systems (design B also constructed of Kel-F).

order rates are observed, rate constants are listed in Table I. Our results in the presence of mono-

TABLE I
EFFECT OF PRESSURE ON THE DECOMPOSITION OF BENZOYL PEROXIDE IN ACETOPHENONE AT 80°

Run	Peroxide concn., mole/liter	P_1 , kg./cm. ²	$k \times 10^5$, sec. ⁻¹	k_{1500}/k_1
1 ^a	0.010	1	5.60	
2	.010	1	5.88	
3	.010	1500	4.56	0.80
4	.046	1	5.53	
5	.046	1	5.53	
6	.046	140	5.17	
7	.046	1500	4.16	0.75
8 ^b	.046	1	4.26	
9 ^c	.046	1	4.26	
10 ^b	.046	1500	3.35	0.79
12 ^a	.10	1	4.99	
13	.10	1	5.06	
14 ^a	.10	140	4.73	
15 ^a	.10	1500	3.95	0.79

^a Acetophenone used without purification (other runs used fractionated material). ^b In presence of 0.3 molar methyl methacrylate. ^c In presence of 0.3 molar styrene.

mers are in good agreement with those of Blomquist and Buselli who give $k = 4.33 \times 10^{-5}$ sec.⁻¹, but they report the same value in acetophenone alone while our results are some 25% higher. We are unable to account for the difference since different acetophenone samples gave essentially the same result.¹² However, since runs at different peroxide concentrations and in the presence and absence of monomer all give good first-order plots and the same pressure coefficient, $k_{1500}/k_1 = 0.78 \pm 0.02$, we believe that we have been successful in isolating the effect of pressure (in this range) on the unimolecular decomposition of benzoyl peroxide. The resulting value of ΔV^\ddagger in the relation

$$d \ln k/dP = -\Delta V^\ddagger/RT \quad (2)$$

is 4.8 cc./mole and identical with that which may be calculated from our measurements in allyl acetate solution at 2500 kg./cm.².⁷ The value appears plausible for a unimolecular dissociation process

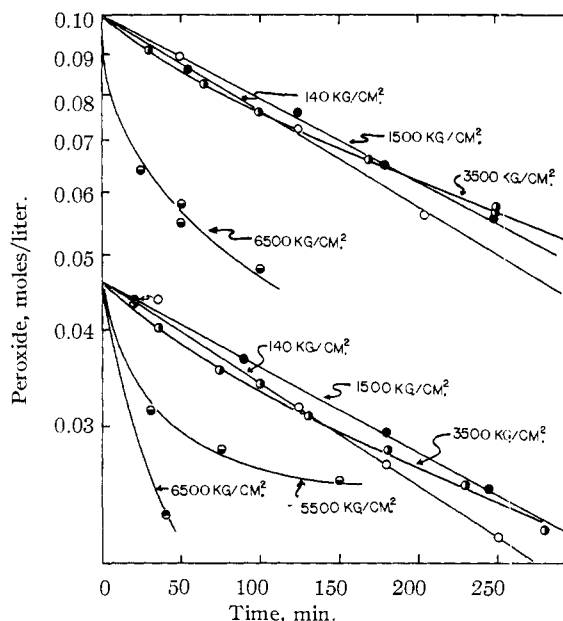


Fig. 2.—Effect of pressure on the rate of decomposition of benzoyl peroxide in acetophenone at 80°.

and is, in fact, almost identical with that for the decomposition of phenylbenzylmethylallylammonium bromide reported by Perrin.¹³

At pressures of 3500 kg./cm.² and above, a

(13) M. W. Perrin, *Trans. Faraday Soc.*, **34**, 144 (1938).

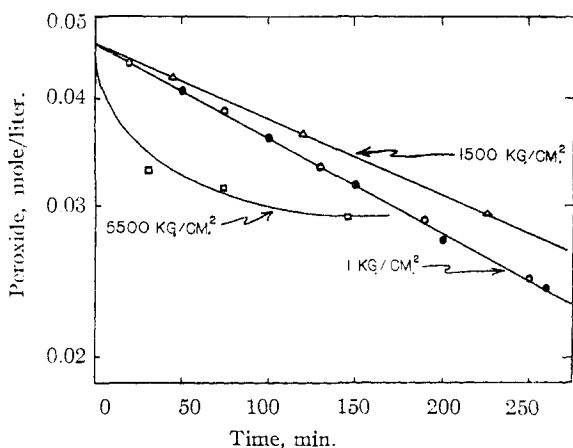


Fig. 3.—Effect of pressure on the decomposition of benzoyl peroxide in acetophenone containing 0.3 molar methyl methacrylate: solid circles, atmospheric pressure run in the presence of 0.3 molar styrene.

striking change in the decomposition of benzoyl peroxide occurs as shown by the curves in Fig. 2 and 3. The reaction rate is now faster than at atmospheric pressure and increases rapidly with pressure. While experimental points are somewhat erratic, particularly at higher pressures, the process appears to be higher than first order. Since we find it hard to conceive of a high-order non-radical process setting in under pressure, we believe that our results indicate the onset of a fast induced chain decomposition of the peroxide. The products of this process have not been determined, so we can say little about its exact nature at present. However, the fact that it occurs equally well in the presence of 0.3 molar methyl methacrylate and also has been noted in allyl acetate⁷ indicates that it is not interrupted by unsaturated molecules acting as radical traps as is the case with at least some of the chain decompositions of benzoyl peroxide at atmospheric pressure.⁹

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

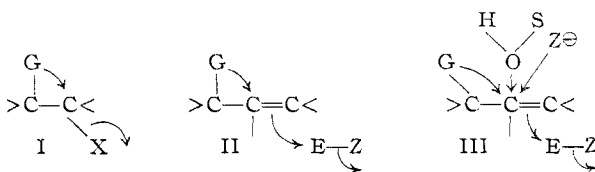
Neighboring Groups in Addition. V.¹ The Benzamido Group in 3-Benzamidopropene²

BY LEON GOODMAN AND S. WINSTEIN

RECEIVED APRIL 3, 1957

The neighboring benzamido group participates effectively in the process of addition of bromine to unsaturated amides. Oxazolinium bromides are major products from addition of bromine to 3-benzamidopropene and 3-*p*-methoxybenzamidopropene in chloroform, methanol or acetic acid as solvent. Neighboring benzamido participation competes with that of solvent or bromide. Since solvent participation depends on solvent nucleophilicity, it is important in methanol and negligible in acetic acid. Bromide participation with resulting dibromide formation can be minimized by use of low reagent concentrations in the addition reaction. It can be eliminated conveniently by the use of *N*-bromosuccinimide as the positive bromine donor. With *N*-bromosuccinimide in acetic acid, where solvent participation is negligible, essentially quantitative yields of oxazoline are obtained.

The close analogy between participation of a neighboring group *G* in nucleophilic substitution I and participation of the same group in electrophilic olefin addition II has been pointed out previously.^{2a}



The primary OH and OAc groups in allyl alcohol and acetate, respectively, fail to participate during bromine or chlorine addition in methanol or water as solvent.³ On the other hand, the *t*-OH group in α,α -dimethylallyl alcohol participates to an easily detectable extent in bromine addition, while the *t*-alkoxide ion group ($-O^{\ominus}$) gives essentially exclusive participation in bromine addition to

α,α -dimethylallyl alcohol.⁴ These observations, as well as others in connection with neighboring carbon,^{1,4} are in qualitative agreement with expectations based on a general correlation¹⁻⁴ between the incidence or importance of neighboring group participation in addition processes and the size of driving forces due to participation in nucleophilic substitution.⁵

Since 2-benzamido-1-cyclohexyl *p*-toluenesulfonate^{2a,6a} and 2-benzamido-1-ethyl toluenesulfonate^{6b} and bromide^{6c} solvolyze very much more rapidly than the corresponding acetoxy derivatives, we can expect the benzamido group to participate in electrophilic olefin addition to a greater extent than the acetoxy neighboring group. More specifically, 3-benzamidopropene offers a more favorable opportunity to observe participation during bromine addition than does allyl acetate. The present paper is concerned with such a study.

3-Benzamidopropene.—Bergmann,^{7,8} who studied

(1) Paper IV, S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56 (1956).

(2) Some of the material of this paper was presented in summary form: (a) S. Winstein, L. Goodman and R. Boschan, *THIS JOURNAL*, **72**, 2311 (1950); (b) S. Winstein, L. Goodman and R. Boschan, p. 436 of Abstracts, XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., Sept., 1951.

(3) S. Winstein and L. Goodman, *THIS JOURNAL*, **76**, 4368 (1954).

(4) S. Winstein and L. Goodman, *ibid.*, **76**, 4373 (1954).

(5) S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

(6) (a) S. Winstein and R. Boschan, *ibid.*, **72**, 4669 (1950); (b) R. Glick, Thesis, U.C.L.A., 1954; (c) F. L. Scott, R. E. Glick and S. Winstein, *Experientia*, **13**, 183 (1957).

(7) M. Bergmann and E. Brand, *Ber.*, **54**, 1645 (1921).

(8) M. Bergmann, F. Dreyer and F. Radt, *ibid.*, **54**, 2139 (1921).