A HIGH PRESSURE STUDY OF THE PHOTOLYTIC DECOMPOSITION OF AZOETHANE AND PROPIONYL PEROXIDE

Inaugural Dissertation

by

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INTRODUCTION

The effect of pressure on rate constants

The study of a chemical reaction under high pressure is a valuable method to elucidate the mechanism of the reaction in that the pressure dependence of the rate constant k for the reaction

$$A + B \rightleftharpoons AB^{*} \longrightarrow \text{Products}$$

yields the volume of activation (1,2,3,4). Knowledge of ΔV^{*}, the volume of activation, together with ΔS^{*}, ΔH^{*} and ΔG^{*}, the entropy, enthalpy and Gibbs free energy respectively of activation, complements our knowledge of the activated complex AB^{*} and facilitate the interpretation of kinetic data.

The equation used to express the relation between the rate constant and the applied pressure was originally derived by Evans and Polanyi (5)

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = - \frac{\Delta V^{*}}{RT} \qquad [1]$$

ΔV^{*} is the volume of activation, i.e. the difference in partial molar volumes between the activated complex and the reactants. P, R and T have their usual significance. The rate constant should be expressed in concentration units invariable with pressure (e.g. molal concentration) to avoid the concentration effect caused by compression.

Acceleration or retardation of a reaction by an increase

in pressure depends on the sign of ΔV^*. Reactions where a bond is broken will generally have a positive ΔV^*, i.e. the activated complex has a larger volume than the reactant and the rate decreases with increasing pressure. Reactions of the type

$$A + B \longrightarrow C$$

will generally involve a decrease in volume and it is reasonable to assume that the volume of the activated complex is less than the volume of the reactants. Such a reaction should have a negative volume of activation and be accelerated by an increasing pressure.

The integrated form of equation 1

$$\ln \frac{k_2}{k_1} = \frac{-\Delta V^* (P_2 - P_1)}{RT} \qquad [2]$$

is valid only in a restricted pressure range, since ΔV^* is variable with pressure. ΔV^* is frequently calculated from the initial slope of a plot $\ln (k_2/k_1) = f(P)$ giving ΔV^* at atmospheric pressure which for all purposes is equal to ΔV^* at zero pressure. However, such a calculation often introduces some ambiguity unless several experimental points at lower pressure are available. The dependence of k on pressure given by the empirical equation

$$\ln k = a + bP + cP^2 \qquad [3]$$

is frequently used to determine ΔV^* from the coefficient b, since

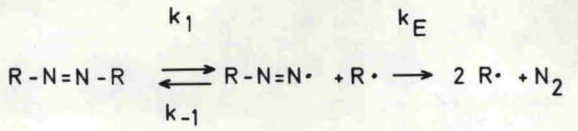
$$b = \frac{-\Delta V^*}{RT} \qquad [4]$$

which can be seen from equation 2.

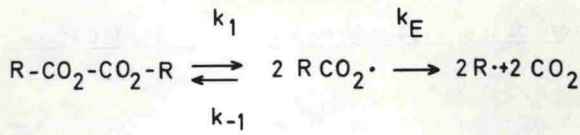
Dissociation of radical precursors and alkyl radical reactions

Radicals are commonly produced in pairs upon photolysis or thermal dissociation of a radical precursor. Elimination of a low molecular weight compound is often involved in these types of reactions. The dissociation of acyclic azo compounds and diacyl peroxides are examples, upon which several review articles have been written (6,7,8). In this study, two compounds, azoethane C_2H_5-N=N-C_2H_5 and propionyl peroxide $C_2H_5CO_2CO_2C_2H_5$ were chosen in order to examine the mechanism of decomposition and the subsequent reactions of the ethyl radicals.

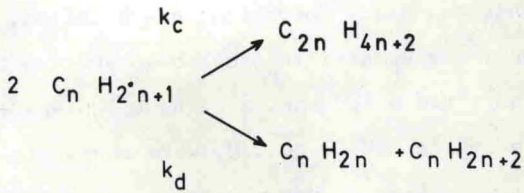
A possible route for decomposition of a symmetrical azo compound in solution is shown in Figure 1 a. The primary formation of an intermediate radical denoted R-N=N· and an alkyl radical R· may, with a certain probability, give way to recombination, unless elimination as described by the rate constant k_E, is much faster than the recombination. The other possible route for decomposition proceeds directly from the parent molecule to the formation of two radicals R· separated by nitrogen. This is accomplished via a simultaneous two-bond scission and is generally called a concerted mechanism in contrast to the earlier described



1a



1b



1c

Figure 1. Formation and reactions of alkyl radicals.
1a. Dissociation of a symmetrical azo compound.
1b. Dissociation of a diacyl peroxide.
1c. Disproportionation and combination of two alkyl radicals.

nonconcerted mechanism.

Figure 1b shows a similar scheme for the decomposition of a symmetrical diacyl peroxide. The primary formation of two intermediate radicals $R\text{-}CO_2^{\cdot}$ in the first step of a nonconcerted mechanism yields upon elimination 2 alkyl radicals and 2 molecules of carbon dioxide. An ester with the

general formula $R\text{-}CO_2\text{-}R$ may also be formed if one of the radicals $R\text{-}CO_2^{\cdot}$ decomposes to an alkyl radical and a carbon dioxide molecule before combining with the other radical. Decomposition of the diacyl peroxides may also follow a concerted mechanism, producing directly, via a simultaneous three-bond scission, two alkyl radicals and two molecules of carbon dioxide.

The actual mechanism for decomposition of these types of compounds is still under discussion. Trapping of the intermediate radical will confirm its existence, however, failure can not exclude the nonconcerted mechanism. It is generally agreed that the thermal dissociation of diacyl peroxides proceeds via a nonconcerted mechanism (7). Several facts support this mechanism, for example the formation of methyl acetate in the thermal dissociation of diacetyl peroxide in solution (9) and the solvent dependence of the rate constant for dissociation (10,11). Since the reported trapping of the acetoxy radical (12) is under discussion (13), the benzoyloxy radical produced in the decomposition of benzoyl peroxide seems to be one of the few intermediate radicals proven by trapping (14). For acyclic azo compounds the stepwise mechanism has been advanced for the thermal decomposition in gas phase (15) and for the photolytic decomposition in solution (16). The nonconcerted process seems to be accepted for the gas phase decomposition, while activation parameters suggest that the decomposition

proceeds by a concerted process in solution (6).

It should be noted that the thermal decomposition and the photolytic decomposition of a radical precursor do not necessarily involve the same steps. It has, for example, been shown by Bevington (17,18) that benzoyl peroxide dissociates thermally into two benzoyloxy radicals. However, upon photolysis approximately 30% of the radicals produced were phenyl radicals. Aliphatic azo compounds will behave differently if they are photolyzed in the gas phase or in solution (19). In the gas phase they will readily decompose to radical products, while in solution the cis-trans isomerization becomes important and the value of the quantum yield of dissociation is much lower than in the gas phase.

The term "cage reaction" of geminate radicals (20,21) refers to the reaction between two radicals formed from the same parent molecule in solution. Originally devised to explain a low quantum yield for the photodissociation of a molecule in solution, compared to that in the gas phase, the theory invokes a cage of solvent molecules which holds the radicals in close proximity to each other leading to a high reaction probability. The rate for a cage reaction would be higher than the rate of the corresponding diffusion controlled reaction. The development of picosecond laser spectroscopy (22) and chemically induced dynamic nuclear polarization (CIDNP) (23) have renewed the interest in cage reactions, in that these techniques put the time-scale for the

event within 10^{-10} seconds. In the propionyl peroxide and azoethane systems the only cage reaction, in the original sense, would be the reverse reaction of the first dissociation step.

Figure 1c shows the competing reactions of two alkyl radicals, which can either be a disproportionation or a combination (24). The question raised with these reactions is whether they involve a common activated complex or proceed through two different complexes. The common activated complex was suggested by Kerr and Trotman-Dickenson (25) but the studies by Benson (26) have led to an acceptance of a scheme involving two different complexes.

For radicals produced in solution the reaction between the radical and a solvent molecule

$$R\cdot + SH \longrightarrow RH + S\cdot$$

producing a solvent radical, can be added to the set of reactions in Figure 1. If a scavenger has been added to the solution, the radical can react with the scavenger, forming either a stable addition product or, by attack on a vinyl group, initiate a polymerization chain.

High pressure studies on dissociation of radical precursors

Dissociation reactions producing radicals were earlier studied under high pressure because of their importance in free radical initiated polymerization. These early investi-

gations are reviewed in reference (1). It was soon recognized that high pressure studies could be used to elucidate the mechanism for the decomposition of this class of compounds. A systematic study was carried out by Neuman (27) who tried to correlate the magnitude of ΔV^* with the mechanism of the decomposition. Several examples of the results from the thermal dissociation of azo compounds and peroxides are given below. The photolytical generation of radicals has attracted less attention, however, examples will be presented.

A general result from these studies is that high pressure will retard the decomposition of the radical precursor. The values for the activation volume of decomposition of benzoyl peroxide varies from 4.7 cm^3/mol in allyl acetate (28) to approximately 10 cm^3/mol in carbon tetrachloride (29). The decomposition of 2,2´-azo-bis-isobutyronitrile in toluene at 60 °C was studied by Ewald (30), who found $\Delta V^* = 3.8$ cm^3/mol when the decomposition was followed directly and $\Delta V^* = 9.4$ cm^3/mol when the decomposition was followed by trapping of the radicals with iodine. The ΔV^* for decomposition of t-butyl peroxide shows a solvent dependence (31) giving the smallest value, 5.4 cm^3/mol, in toluene and the largest value, 13.3 cm^3/mol, in carbon tetrachloride. This result stresses the fact that the ΔV^* observed for decomposition is not necessarily the ΔV^* for breaking of the particular bond involved in the dissociation.

Neuman studied several radical precursors under high pressure, mainly azo compounds (27). He divided the precursors in two groups, those showing a small observed ΔV^* for decomposition (4-5 cm^3/mol) and those showing a large ΔV^* (>10 cm^3/mol). A large ΔV^*, it was reasoned, should be characteristic for a nonconcerted process, during which recombination could occur, whereas a small ΔV^* should indicate a concerted mechanism. According to this scheme, azo-bis-isobutyronitrile, azocumene and a few other azo compounds would decompose by a two-bond scission, while benzoyl peroxide and para-nitrophenyl-azotriphenylmethane, showing large ΔV^*, would decompose by a one-bond scission. However, the solvent effect on ΔV^* for benzoyl peroxide and t-butyl peroxide casts some doubt on the general validity of this classification.

In the study by Vogt and Hamill (32) on the thermal decomposition of acetyl peroxide under high pressure, no attempt was made to determine the rate constant for decomposition. At higher pressure, an increase in the amount of methyl acetate formed was demonstrated, which they ascribed to an enhancement of the reaction

$$CH_3CO_2^{\cdot} + CH_3^{\cdot} \longrightarrow CH_3CO_2CH_3$$

Correspondingly, few studies have been made on the photolytic decomposition of these types of compounds under high pressure. Nicholson and Norrish (33) in their study of the

polymerization of styrene decomposed benzoyl peroxide with light. They found no effect of pressure on the initiation rate. Azo-bis-isobutyronitrile has been photolyzed in toluene at room temperature (34) and the rate of decomposition measured by following the rate of disappearance of diphenylpicrylhydrazyl. The observed activation volume was 7.6 cm^3/mol.

Internal pressure and radical reactions

Attempts to correlate the ratio of the rate constants of disproportionation and combination, k_d/k_c, of ethyl radicals with the internal pressure of the solvent was made by Dixon et al. (35) with good correlation. However, in a later study by Sheldon and Kochi (36) where aliphatic diacyl peroxides were photolyzed, it was found that k_d/k_c was the same in gas phase and in the solvents pentane and decalin. Neuman (37) also failed to observe a correlation between the rate of decomposition of radical precursors and the internal pressure of the solvent.

At present, it appears that values of the activation volume must be calculated from high pressure measurements rather than from solvent parameters, although the interesting results by Dixon et al. may warrant further research in this field.

Description of the present investigation

The main objective of this investigation was to study the change in the quantum yield of decomposition of azoethane and propionyl peroxide with pressure. From the change in quantum yield it should be possible to calculate ΔV^* for decomposition and its magnitude would, hopefully, make it possible to differentiate between a concerted and nonconcerted mechanism.

The relative rates between disproportionation and combination of ethyl radicals should be affected by pressure and make it possible to calculate the difference in ΔV^* between the two activated complexes.

The investigation is comprised of three parts. Two of these parts deal with the photolysis of azoethane, the third deals with the photolysis of propionyl peroxide.

The first study of the azoethane photolysis, published in 1970 (38), deals with the photolysis of azoethane under pressure in toluene and 2,2,4-trimethyl pentane with 1,1-diphenyl ethylene as an added scavenger. The objective of this work was to establish the change in the k_d/k_c ratio with an applied pressure, which was accomplished by measuring the relative amount of hydrocarbons formed during the photolysis. In the following, this study is referred to as "the first azoethane study". This work was later extended to include a study of the photolysis of azoethane in 2,2,4-trimethyl pentane without scavenger. This study

is referred to as "the second azoethane study" and was concerned with the change in quantum yield of decomposition with pressure and the effect of pressure on the ethane/ethylene ratio. The absolute amount of hydrocarbons formed was determined as was the amount of light entering the photolysis cell. In order to estimate the number of ethyl radicals not reacting with other ethyl radicals, a set of experiments was also performed, using di-tert-butyl nitroxide as a scavenger.

"The propionyl peroxide study" was also made in order to establish the effect of pressure on the quantum yield of decomposition, the solvent again being 2,2,4-trimethyl pentane. The absolute amounts of carbon dioxide and hydrocarbons were determined, with the quantum yield at high pressure determined relative to the quantum yield at atmospheric pressure. Nitric oxide was used in some experiments as a scavenger yielding information as to the cage effect in this system.

EXPERIMENTAL

Outline of the experimental technique

The experimental technique was similar in the different studies. The appropriate solution was prepared and introduced into the photolysis cell under high vacuum. The solution was compressed in the high pressure vessel and photolyzed. After the photolysis the solution was distilled on the vacuum line and the gaseous products separated from the solution and collected in an ampoule. The contents of this ampoule were analyzed on a gas chromatograph.

The details of the technique used in the different studies will be given after the description of the materials and apparatuses used.

Materials

Azoethane (Merck, Sharp and Dohme) was refluxed and distilled under vacuum to remove any low molecular weight hydrocarbons.

Propionyl peroxide was prepared by the acyl chloride-H_2O_2-pyridine method described by Kochi and Mocadlo (39). The purity of the peroxide was checked by iodometric titration, a method described by Wagner et al. (40). In all experiments the purity of the peroxide exceeded 98%.

2,2,4-trimethyl pentane, spectroscopic grade (E. Merck AG) was refluxed with CaH_2, distilled and finally refluxed under

vacuum to remove traces of any low molecular weight hydrocarbons.

Toluene, p.a., (E. Merck AG) was refluxed with CaH_2 and distilled.

1,1-diphenyl ethylene, 97%, (Aldrich Chem. Co.) was distilled under reduced pressure and the middle fraction retained.

Di-tert-butyl nitroxide (DTBN) was prepared by the method of Hoffman and co-workers (41). The nitroxide was purified on a semi-preparative gas chromatograph (Varian P-90) equipped with a 2.5 m column of Chromosorb W with 15% SE-30.

Nitric oxide, C.P. (Matheson Co.).

Propane, C.P. (J.T. Baker Chemical Co.) was proved by gas chromatography to be 98% pure, the impurity being ethane.

The absorption spectra of azoethane and propionyl peroxide are shown in Figure 2.

The photolysis equipment

In the first azoethane study the photolysis arrangement was a Philips high pressure mercury lamp, placed under the high pressure vessel, with aluminium foil to provide a light guide. Wave-lengths below 340 nm were excluded by a cut-off filter. Since this study was only concerned with the relative amount of hydrocarbons formed in each photolysis, the amount of light entering the cell was not determined in each

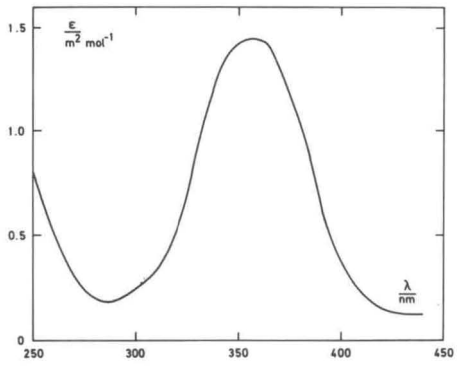


Figure 2a. The absorption spectrum of azoethane in 2,2,4-trimethyl pentane.

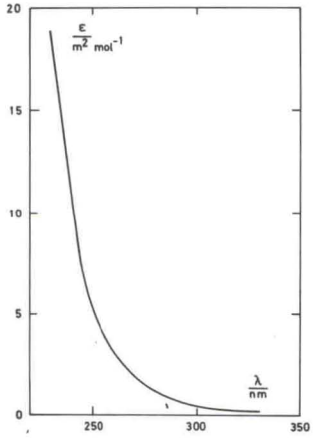


Figure 2b. The absorption spectrum of propionyl peroxide in 2,2,4-trimethyl pentane.

experiment. In a separate experiment the flux into the photolysis cell was determined to be $2 \cdot 10^{17}$ quanta/sec measured with an uranyl oxalate actinometer. The light intensity from the high pressure mercury lamp decreased slowly with time, the flux into the cell within a month varying between $1 \cdot 10^{17}$ - $3 \cdot 10^{17}$ quanta/sec.

In the second azoethane study the flux into the photolysis cell was determined in each experiment in order to estimate the quantum yield of decomposition of azoethane. This was accomplished by introducing a reference cell with a ferri oxalate actinometer into the photolytic system.

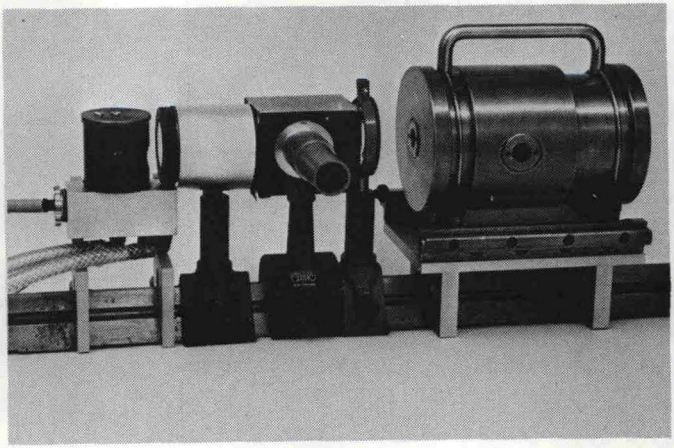


Figure 3. The photolysis system used in the second azoethane study.

The photolysis arrangement is shown in Figure 3. It consisted of a high pressure mercury lamp and a lens to allow parallelization of light through the metal housing (see Figure 4), containing a transmission filter, (λ = 365 nm at T_{max}), and a semi-reflecting quartz plate. After passage

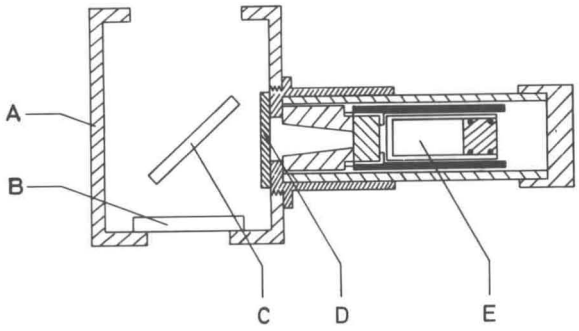


Figure 4. Metal house for splitting of the photolysis light and the holder for the reference cell.
A. Metal house. B. Transmission filter.
C. Quartz plate. D. Neutral density filter.
E. Quartz cell for reference solution.

through the housing the light was focused by a lens into the photolysis cell and 15% of the light entering the housing was reflected 90° by the quartz plate. Because of the great difference in quantum yield for the ferri oxalate actinometer used, ϕ = 1.21 (42), and the quantum yield

of decomposition for azoethane, ϕ = 0.02 (16), a neutral density filter consisting of a copper net was introduced in front of the actinometer. The ratio between the amount of light entering the photolysis cell and the reference cell containing the actinometer solution was determined to be 230 to 1. The cell for the actinometer was of the same type as the photolysis cell and surrounded by a metal holder to exclude stray light.

In the propionyl peroxide study, a Philips medium pressure mercury lamp was used to decompose the peroxide. A 5 cm quartz cell with a $CoSO_4$ - $NiSO_4$ filter solution (43) was incorporated into the system, allowing maximum transmission at λ = 280 nm. Since the output from the medium pressure mercury lamp was fairly constant, it was not necessary to determine the amount of light entering the cell in each experiment.

The high pressure equipment

The high pressure equipment used in this study has been described in detail by Claesson et al. (44). Only a short description will be given here.

The pressure vessel (Figure 5) consisted of a steel cylinder with a central hole and a radial channel both of which could be closed at the ends with O-ring sealed pistons supported by screws. The bottom piston (A) was channeled to provide an entrance for the photolysis light. The surface

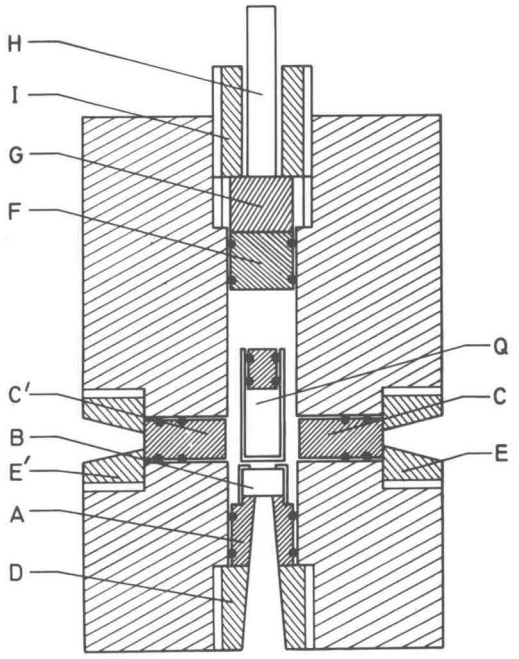


Figure 5. High pressure vessel. A. Steel piston. B. Sapphire window. C,C′ Solid steel piston. D. Bottom screw. E,E′ Screw for side piston. F. O-ring sealed top piston. G. Distance piece. H. Steel rod. I. Top screw. Q. Photolysis cell.

of the piston facing the inside of the vessel was polished and a sapphire window (B) was placed on the surface, giving a seal of the conventional unsupported type. A threaded steel cap held the sapphire window in position before pressure was applied. The bottom piston was locked by the screw

(D) which also was channeled. The side windows (C and C′) were made of solid steel and held in place by screws (E and E′). When absorption measurements were made, however, the solid steel pistons were replaced by pistons with sapphire windows. The photolysis cell (Q) consisted of a cylindrical quartz tube with a flat bottom window. The cell was filled under vacuum with solution (see below) and closed with a movable aluminium plunger, equipped with two O-rings. The O-rings provided a seal between the test solution and the pressure transmitting medium while preventing gases formed in the photolysis to escape from the solution. The photolysis cell was secured in the middle of the vessel by a specially designed holder (not shown in Figure 5) and surrounded by a pressure transmitting medium, which generally was glycerol. When pressure was applied, the vessel was attached to a hydraulic press and the O-ringed plug (F) and distance piece (G) were driven into the vessel by the rod (H). The pressure transmitting medium was compressed and the pressure was transmitted to the sample solution by the downward movement of the aluminium plunger in the photolysis cell. When the desired pressure was reached, the distance piece (G) was locked in its position by the upper screw (I). The vessel was then disconnected from the press and taken to the photolysis apparatus. The hydraulic press was equipped with a Bourdon gague which had been accurately calibrated by a piezometric method (45) so the pressure inside the

vessel was known with $\pm$2.5% accuracy.

The high vacuum equipment

The high vacuum line was a conventional all-glass apparatus equipped with a mechanical pre-vacuum pump and a mercury diffusion pump. Ground glass stop-cocks or teflon stop-cocks were used. The vacuum attainable was 2 mPa. The sections of the vacuum line deserving special description allowed preparation of the ampoules with azoethane solution and separation of the gas products from the solvent after the sample solutions had been photolyzed. The cells used in the high pressure vessel were filled and opened under vacuum. The apparatus necessary for these manipulations is also described.

The section of the vacuum line used for preparing ampoules with azoethane solution is shown in Figure 6. It consisted of a blackened glass cylinder (A) for azoethane storage, a mercury manometer (B), a glass flask of known volume (C), connection to a high vacuum line (D) and a ground joint (E) for attachment of solvent ampoules. After degassing of the solvent by the freeze-and-thaw technique, the stop-cocks (F,G) were closed and the stop-cocks (H,I,K) opened. The glass flask was filled with azoethane to the desired pressure and the stop-cock (H) closed. Excess azoethane was distilled back into the storage cylinder and the stop-cock (K) was closed. The stop-cocks (H,F) were then

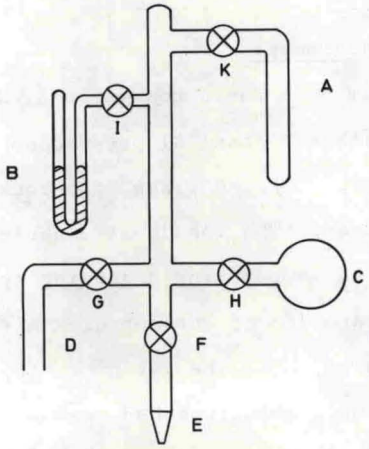


Figure 6. Part of the vacuum line used to prepare ampoules with azoethane solution. A. Storage cylinder for azoethane. B. Mercury manometer. C. Flask of known volume. D. Connection to high vacuum line. E. Ground joint. F,G,H,I,K. Teflon stopcock.

opened and azoethane was distilled down into the solvent ampoule after which it was sealed off.

The section of the vacuum line used for separating the gases from the photolyzed solution is depicted in Figure 7, together with two types of ampoules used for gas collection. It consisted of the following parts: a ground joint (A) for attachment of the cell-opening device, a condenser (B), a

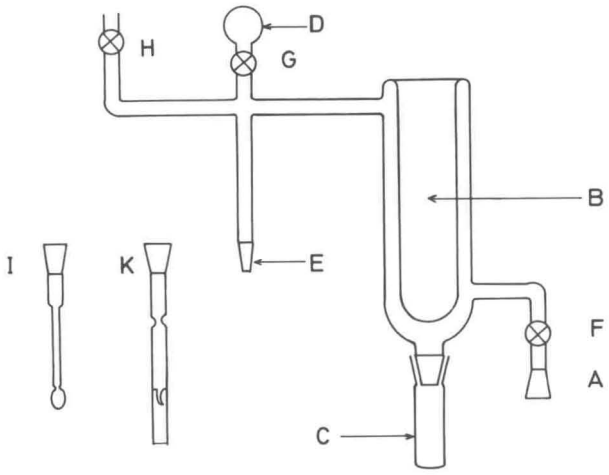


Figure 7. Part of the vacuum line used for separating gas products from the solvent. A. Connection for the cell opening device. B. Condenser. C. Glass tube. D. Flask of known volume. E. Connection for gas ampoules. F,G,H. Teflon stop-cock. I,K. Ampoules for collecting gas.

glass tube (C) under the condenser, a glass flask of known volume (D) and a ground joint (E) for attachment of the gas collecting ampoules. The apparatus was used in the following way: after the apparatus for opening the cell was connected and the entire section was evacuated, the stop-cock (H) was closed. The condenser was filled with liquid nitrogen and the photolysis cell was opened. The test solution was distilled from the cell through the stop-cock (F) and trapped on the condenser. If azoethane was the radical precur-

sor, nitrogen was pumped of the system by opening the stop-cock (H) after the temperature of the condenser had been decreased to 60 K by letting nitrogen in the condenser boil under reduced pressure. Upon transference of the material from the cell to the condenser, the solution was thawed and collected in the glass tube (C). The condenser was then filled with a solid carbon dioxide-2-propanol cold bath and the gas collection ampoule (I) or (K), connected at (E), was cooled at 77 K. In this way, the solvent, refluxing under vacuum, was condensed on (B) and dripped back into the tube. The gases distilled through the condenser and were condensed in the gas collection ampoule. If the absolute amount of gas was to be determined, a known amount of propane was transferred from the glass flask of known volume (D) to the gas ampoule.

The apparatus used for filling the photolysis cell has already been described by Claesson et al. (46). It consisted of a glass vessel and a teflon stopper (D) shown in Figure 8. The stopper had three holes, one for the glass tubing (A), to which an ampoule with solution was sealed, one for the movable rod (B) with the aluminium plunger, and one for the center axis to which the cell (F) was attached. The rods were sealed to the teflon with rubber O-rings. The apparatus was assembled as shown and evacuated. Upon attainment of a good vacuum, the system was closed by a stop-cock. The cell was filled to 2/3 with solution and

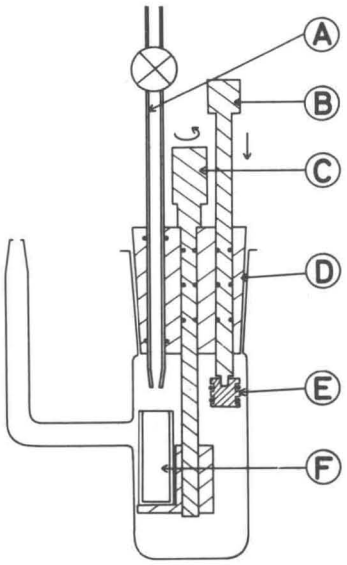


Figure 8. Device for filling high pressure cells under vacuum. A. Glass tube with stop-cock for the solution. B,C. Steel rod. D. Teflon stopper. E. Aluminium plunger. F. Holder with photolysis cell.

rotated half a turn. Thereafter the plunger (E) was pressed into the cell. After disconnecting the glass vessel from the vacuum line, the teflon stopper was lifted and the cell was ready to be placed in the high pressure vessel.

After the photolysis, the cell was opened in vacuum with the apparatus shown in Figure 9. This apparatus also consist-

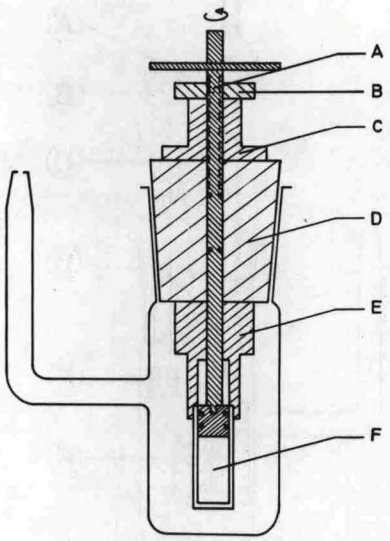


Figure 9. Device for opening high pressure cells. A. Threaded steel rod. B. Nut. C. Aluminium holder. D. Teflon stopper. E. Cell holder. F. Photolysis cell with plunger.

ed of a glass vessel with a teflon stopper through which a hole had been drilled for the steel rod (A). Two rubber O-rings provided the seal between the movable rod and the stopper. The cell (F) was mounted in the way indicated in the figure. The rod was passed through the aluminium holder (C), the teflon stopper and the holder for the cell (E). The end of the rod was screwed into the aluminium plunger in the high pressure cell. The glass vessel was attached

to the vacuum line and evacuated. By turning the nut (B) the threaded steel rod pulled out the plunger distilling the solution into the vacuum line.

The analytical equipment

The device to transfer gases from the gas ampoule to the chromatograph is shown in Figure 10. It consisted of a length of glass tubing to which the ampoule (E) was sealed,

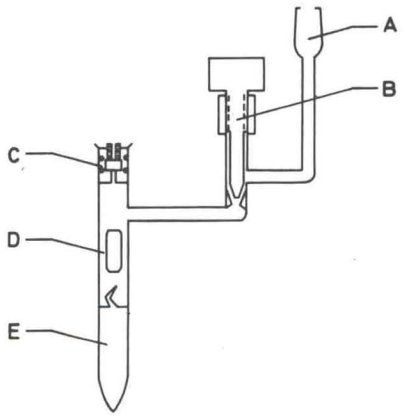


Figure 10. Device for opening gas ampoules. A. Ground joint. B. Teflon stop-cock. C. Metal stopper with rubber septum. D. Hammer. E. Gas ampoule.

a teflon stop-cock (B) and an O-ring-sealed stopper with a rubber septum (C). After the device had been evacuated

and the stop-cock closed, the ampoule was opened by crushing the breakseal with the hammer (D). A sample was then withdrawn by penetrating the rubber septum with a gas tight syringe and then injected into the gas chromatograph. This device was used in the propionyl peroxide study and in the second azoethane study.

In the first azoethane study the tiny gas ampoule (see Figure 7, part I) was placed in a piece of PVC-tubing, connected to the carrier gas stream. The sample was then introduced into the chromatograph by crushing the ampoule with a hammer.

Two different gas chromatographs have been used in this work, a Varian Aerograph 600 in the first azoethane study and a F & M Scientific Corporation research gas chromatograph 810 in the second azoethane study and in the propionyl peroxide study. The Aerograph was equipped with a 5 mm x 2 m glass column packed with Al_2O_3 + 2% dinonyl phtalate, 30-60 mesh. Column temperature: 20 ± 3 °C. Carrier gas: N_2, flow rate 50 cm^3/min. Detector: Flame ionization detector.

In the second azoethane study, a 1/4" x 2 m stainless steel column was connected to the flame ionization detector of the F & M 810. The packing material was silica gel 60-100 mesh. The chromatographic data were the following: Carrier gas: N_2, flow rate 120 cm^3/min. Injector temperature: 100 °C. Oven temperature: 50 °C. The chromato-

gram (Figure 11) shows a typical analysis of a sample photolyzed for 12 hours. 1.49 μmol of propane was added to the sample as an internal standard.

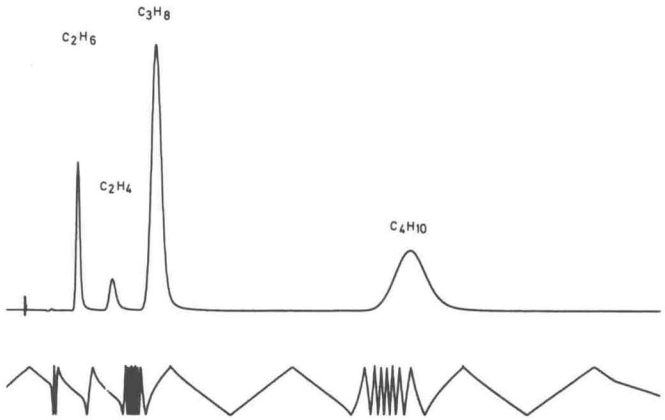


Figure 11. Gas chromatogram of low molecular weight hydrocarbons on a 2 m silica gel column. Flame ionization detector, carrier gas N_2, flow: 120 cm^3/min, oven temperature: 50 ^oC.

In the propionyl peroxide study the thermal conductivity detector of the F & M was used. The column was 1/4" x 1 m stainless steel column packed with Porapak R, 80-100 mesh. The chromatographic data were the following: Carrier gas: He, flow rate 120 cm^3/min. Injector temperature: 150 ^oC. Detector temperature: 250 ^oC. Bridge current: 200 mA. Oven temperature: 50 ^oC for 1 minute, 50-120 ^oC with a temperature

increase of 30 °C per minute and isothermal 120 °C for four minutes. The gas chromatogram in Figure 12 shows a typical analysis of a sample from a 2 hour photolysis at one atm pressure with 13.9 μmol propane added as an internal standard.

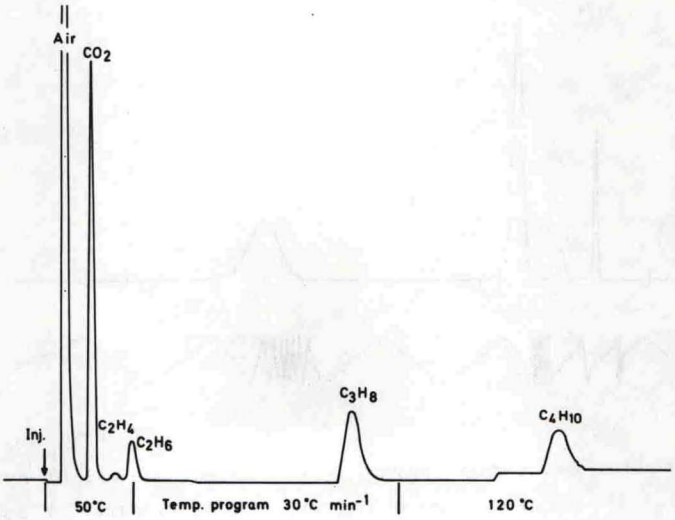


Figure 12. Gas chromatogram of low molecular weight hydrocarbons on a 1 m Porapak R column. Thermal conductivity detector, carrier gas He, flow 120 cm^3/min, temperature program as indicated.

Description of the experimental technique

The experimental technique employed in the first azoethane study was the following: The purified solvent, toluene or 2,2,4-trimethyl pentane, both with one mole per

cent of 1,1-diphenyl ethylene, was introduced into a glass ampoule equipped with a break-seal and a ground joint. The ampoule was then connected to the part of the vacuum line used for preparing ampoules with azoethane solution (Figure 6). After three successive freeze-and-thaw cycles, the solution was degassed and azoethane was added to the solution. The azoethane concentration was in all experiments 5 mol m^{-3}. The ampoule was sealed off from the vacuum line and sealed to the glass tubing in the apparatus used for filling high pressure cells. The apparatus was assembled, evacuated and the break-seal was opened with a hammer. After the photolysis cell had been filled and closed with the plunger, it was transferred to the high pressure vessel. The solution was photolyzed for 12 hours, the temperature being approximately 35 ^{o}C upon which 10-30% of the azoethane was decomposed during the photolysis. After photolysis the cell was placed in the device used for opening high pressure cells, opened and the solution was distilled into the vacuum line. The gases were separated from the solvent, unphotolyzed azoethane and scavenger by refluxing for one hour. The small gas collection ampoule was sealed off and its contents analyzed. The areas of the peaks on the gas chromatogram were determined by planimetry and the ratios between the hydrocarbons were calculated. The appropriate response factors given by Dietz (47) were introduced in the calculations.

In the second azoethane study, the ampoules with azoethane solution were prepared as described above. The solvent was 2,2,4-trimethyl pentane and the concentration was 20 mol m^{-3}. In several experiments di-tert-butyl nitroxide at a concentration of 5.85 mol m^{-3} was added directly to the solvent and the cell filled in the usual manner. The photolysis was conducted with a ferri oxalate actinometer in the photolytic system. About 5% of the azoethane was photolyzed during a 12 hour photolysis at a temperature of 22 ± 2 °C. After the gases had been separated from the solution and collected in the gas ampoule a known amount of propane was added as an internal standard and analyzed with the F & M gas chromatograph. From the integration trace of the recorder, the areas of the peaks could be determined. After introduction of the appropriate response factors, the absolute amount of gases formed in the photolysis could be determined. Since the amount of light entering the photolysis cell was known, the quantum yield of formation of low molecular weight hydrocarbons could be calculated. When di-tert-butyl nitroxide had been added to the solution, the amount of nitroxide disappearing under photolysis was determined by absorption measurement done directly in the high pressure vessel. The nitroxide is a convenient scavenger in this system from the optical point of view since it has a minimum absorption in the 360 nm region where azoethane is absorbing. The peak at 465 nm, where $\varepsilon = 0.89$ $m^2 mol^{-1}$, was used to deter-

mine the change in concentration of the nitroxide.

The propionyl peroxide photolyses were performed in the following way: A 200 cm^3 11 mol m^{-3} solution was prepared in an ampoule and the ampoule connected to the high vacuum line. The solution was cooled with a solid carbon dioxide--2-propanol bath and evacuated until the pressure in the ampoule was less than 2 Pa. Then the ampoule was sealed off and the solution was divided under vacuum into 5 ampoules, each containing 40 cm^3 of solution. The concentration of the solution was chosen as to minimize the radical induced decomposition of the peroxide. A check of the carbon dioxide content in the solution proved it to be approximately 0.5% of the amount of carbon dioxide produced in an ordinary run. In those experiments where NO was added as a scavenger, it was added from the vacuum line to the solution by condensing the gas with liquid nitrogen. The concentration of NO was 1 mol m^{-3}. The high pressure cell was filled in the usual way, placed in the high pressure vessel and photolyzed by the filtered light from the medium pressure mercury lamp. To minimize the effect of long-time drift in the intensity of the light from the lamp and fluctuation in the transmission of the filter solution, the different photolyses were performed in sets in the following way: The same stock solution was used throughout a single set and stored in a refrigerator between the fillings of the photolysis cell to ensure that no thermal decomposition of the peroxide

occurred. The yield of carbon dioxide at 1 atm pressure was taken as a standard value, and the results from the subsequent photolyses at elevated pressures were compared to this standard value. A set generally consisted of 2-4 photolyses of which two photolyses were made each day. The photolysis time was 2 hours and the temperature 21$\pm$ 2 ^{o}C. Under an ordinary photolysis approximately 30% of the peroxide was decomposed. After the photolysis, the gases were separated from the solution, the internal standard was added and the sample analyzed. The peak areas were determined by the cut-and-weigh method from which the absolute amounts of gases formed were calculated after introduction of the proper response factors.

The calculation of quantum yield at high pressure

The quantum yield of a photochemical reaction is defined as the number of molecules reacted, divided by the number of photons absorbed

$$\phi = \frac{n}{I(1-10^{-\varepsilon(A)l})} \qquad [5]$$

where ϕ is the quantum yield, n is number of molecules reacted, I the number of photons entering the cell, ε the absorption coefficient, (A) the concentration of absorbing species and l the optical path length.

It has been assumed that the amount of light entering the photolysis cell at higher pressure is the same as the

amount entering the cell at atmospheric pressure. Although not rigorously true, the difference is very small and arises from two factors: change in the transparency of the materials in the optical path and changes in reflection losses at the different interfaces from changes in refractive indices with pressure. The first factor is not important since the absorption of the materials in the light path (the sapphire window, the pressure transmitting medium and the quartz in the bottom of the photolysis cell) is unaffected by pressure. The second effect is of minor importance, which can be seen from the following arguments. The greatest loss arises at the interface air-sapphire. This loss is approximately 8% and is not affected by pressure. The losses at subsequent interfaces are of the order 1% or less. If the refractive index of glycerol and 2,2,4-trimethyl pentane is increased by 7% when the pressure is increased to 500 MPa, the result will be that 0.5% more light will enter the cell at the higher pressure compared to atmospheric pressure.

In a cell with cylindrical symmetry, the fraction of light absorbed (the second term in the denominator of equation [5]) is unaffected by pressure if the absorption coefficient ε is unaffected by pressure. This was checked for both azoethane and propionyl peroxide and it was found that changes in absorption could be wholly ascribed to concentration changes when the solution was compressed. Compression data given by Bridgman (48) were used in these

calculations.

Consequently, ϕ at high pressure can be determined from the number of molecules reacted, if I at atmospheric pressure is known. Alternatively, ϕ at high pressure can be determined relative to ϕ at atmospheric pressure from the ratio between the number of molecules reacted, if I is the same during two photolyses.

RESULTS

In this section the results from the different studies are given in tables and diagrams. The significance of these results is discussed in the next section.

Results from the first azoethane study

The pertinent ratios between hydrocarbons formed are presented in Tables I (photolysis in 2,2,4-trimethyl pentane) and II (photolysis in toluene). It can be seen from both the Tables and Figure 13 that the ratio $(C_2H_4)/(C_4H_{10})$

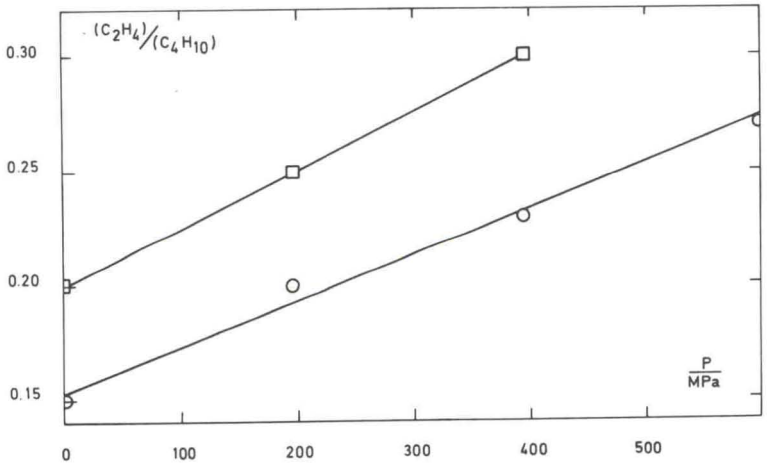


Figure 13. The ratio $(C_2H_4)/(C_4H_{10})$ as a function of pressure.

□ Azoethane in toluene with 1,1-diphenyl ethylene.

○ Azoethane in 2,2,4-trimethyl pentane with 1,1-diphenyl ethylene.

increases with increasing pressure while the ratio $(C_2H_6)/(C_2H_4)$ is approximately one and unaffected by pressure. Assuming that butane and ethylene are formed only through the cross reactions between ethyl radicals, it is possible to calculate the difference in volume of activation. The absolute rate constants of the disproportionation and combination have not been determined, only the ratios between them. Therefore the ΔV^* calculated will be the difference in volume of activation between disproportionation and combination. The plot $\ln(k_d/k_c)$ as a function of pressure is shown in Figure 14, and by fitting the data to equation

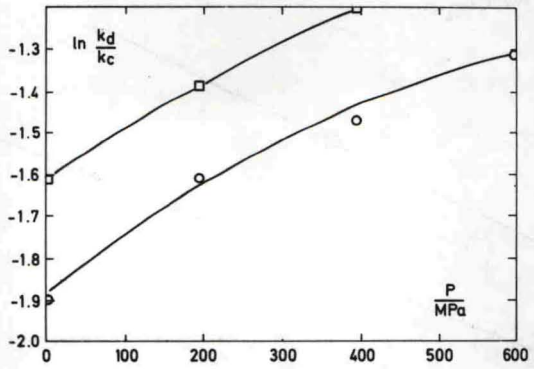


Figure 14. The effect of pressure on $\ln(k_d/k_c)$.
□ Azoethane in toluene with 1,1-diphenyl ethylene.
○ Azoethane in 2,2,4-trimethyl pentane with 1,1-diphenyl ethylene.

[3], (ΔV_c^* - ΔV_d^*) can be calculated from the constant b. The difference calculated in this way is 3.7 cm^3/mol in 2,2,4-trimethyl pentane and 3.2 cm^3/mol in toluene.

Table I

The ratio between hydrocarbons formed in the photolysis of azoethane at different pressures. Concentration of azoethane = 5 mol m^{-3}. Solvent: 2,2,4-trimethyl pentane with 1,1-diphenyl ethylene. Temperature: 35 °C.

Pressure /MPa		$(C_2H_4)/(C_4H_{10})$	$(C_2H_6)/(C_2H_4)$
0.10		0.14	1.5
"		0.15	1.2
"		0.15	1.3
"		0.15	1.1
	Average	0.15	1.3
195		0.20	1.0
"		0.20	1.1
"		0.21	1.0
	Average	0.20	1.0
395		0.25	1.4
"		0.21	1.4
"		0.23	1.6
"		0.22	1.1
	Average	0.23	1.4
598		0.27	1.0
"		0.28	1.1
"		0.25	1.2
	Average	0.27	1.1

Table II

The ratio between hydrocarbons formed in the photolysis of azoethane at different pressures. Concentration of azoethane = 5 mol m^{-3}. Solvent: Toluene with 1,1-diphenyl ethylene. Temperature: 35 °C.

Pressure /MPa		$(C_2H_4)/(C_4H_{10})$	$(C_2H_6)/(C_2H_4)$
0.10		0.20	1.2
"		0.20	1.1
"		0.20	1.2
	Average	0.20	1.2
195		0.24	1.0
"		0.25	0.93
"		0.26	1.2
	Average	0.25	1.0
395		0.30	0.95
"		0.31	0.94
"		0.28	1.1
	Average	0.30	1.0

Results from the second azoethane study

These results have been collected in Tables III-VI. In Table III the μmol products formed during the 12 hour photolysis are listed together with the amount of light that entered the photolysis cell. The ratios between the various hydrocarbons formed are presented in Table IV together with the quantum yield of formation of low molecular weight hydrocarbons denoted ϕ_{FH}. The quantum yield was calculated assuming that the fraction of light absorbed was unity. It can again be seen that the ratio $(C_2H_4)/(C_4H_{10})$ increases with an increase in pressure, as in the first azoethane study, while the quantum yield for formation of low molecular weight hydrocarbons and the ratio $(C_2H_6)/(C_2H_4)$ decreases with pressure. The pressure dependence on the ratio $(C_2H_4)/(C_4H_{10})$ is shown in Figure 15.

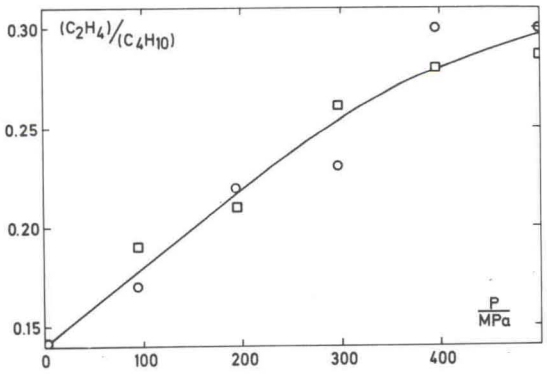


Figure 15. The ratio $(C_2H_4)/(C_4H_{10})$ as a function of pressure. Ethyl radical source: Azoethane in 2,2,4-trimethyl pentane. ○ No scavenger added. □ DTBN used as a radical scavenger.

The plot $\ln(k_d/k_c)$ as a function of pressure is given in Figure 16 and the difference in volume of activation, again calculated by use of equation [3], is 4.4 cm^3/mol. No scavenger was added in this set of experiments. However, the difference in volume of activation when di-tert-butyl nitroxide was added differed only slightly from the previous value, being 4.6 cm^3/mol.

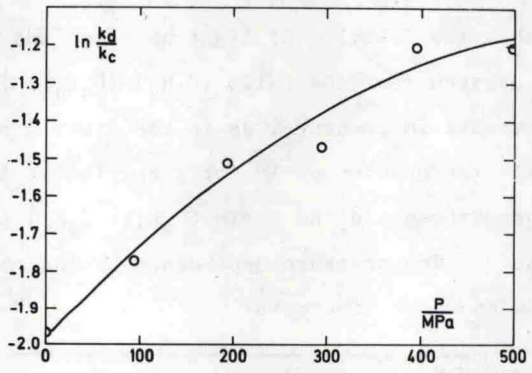


Figure 16. The effect of pressure on $\ln(k_d/k_c)$. Ethyl radical source: Azoethane in 2,2,4-trimethyl pentane without scavenger.

The quantum yield for formation of low molecular weight hydrocarbons (ϕ_{FH}) listed in Table IV have been plotted in Figure 17. In Table V the results from the photolysis of azoethane with di-tert-butyl nitroxide are listed. Again the number of μmol products formed during the 12 hour photolysis is given together with the number of quanta absorbed.

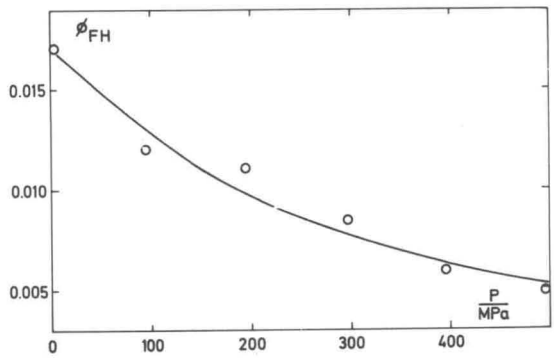


Figure 17. Quantum yield of decomposition of azoethane as a function of pressure. The quantum yield has been calculated from the formation of low molecular weight hydrocarbons. Solvent: 2,2,4-trimethyl pentane without scavenger.

The amount of di-tert-butyl nitroxide reacted as determined from spectrophotometric measurements is also given. The pertinent ratios from these experiments are listed in Table VI together with ϕ_{FH} and ϕ_{FE} (ϕ_{FE} = quantum yield for formation of ethyl radicals) calculated from the amount of hydrocarbons formed plus the amount of reacted nitroxide. The graphic representation of these data is shown in Figure 18, where ϕ is plotted against pressure, ϕ_{FE} and ϕ_{FH} being the upper and lower curve respectively. A plot of $\ln\phi_{FE}$ as a function of pressure is given in Figure 19. The value for the ΔV^* for decomposition is 5.7 cm^3/mol calculated from the

constant b in equation [3].

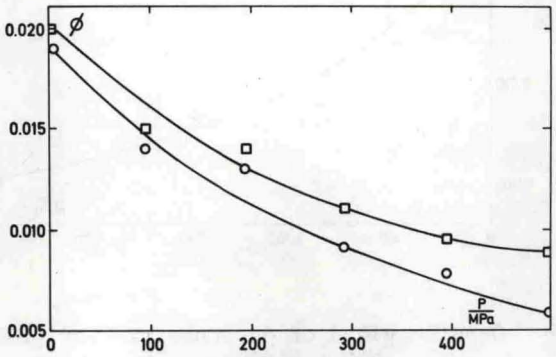


Figure 18. Quantum yield for decomposition of azoethane as a function of pressure. Solvent: 2,2,4-trimethyl pentane with di-tert-butyl nitroxide as a scavenger.

- O ϕ calculated from the formation of low molecular weight hydrocarbons.
- □ ϕ calculated from the formation of low molecular weight hydrocarbons plus the change in concentration of DTBN.

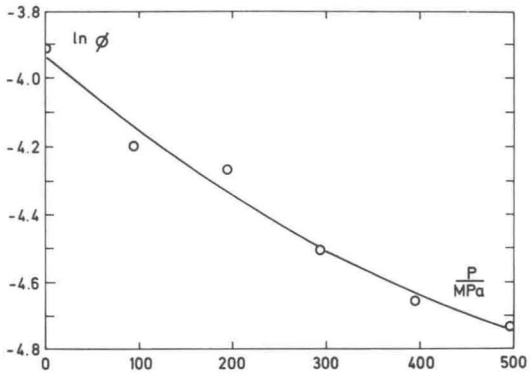


Figure 19. The effect of pressure on lnϕ for decomposition of azoethane.

Table III

Results from the photolysis of azoethane in 2,2,4-trimethyl pentane at different pressures. Concentration of azoethane. 20 mol m^{-3}. Temperature: 22±2 °C.

Pressure /MPa	Products formed/μmol C_2H_6	C_2H_4	C_4H_{10}	Quanta absorbed /μeinstein
0.10	0.99	0.24	1.7	144
"	0.68	0.21	1.5	111
"	0.91	0.30	2.1	153
95	0.41	0.17	0.99	125
"	0.50	0.21	1.3	126
"	0.54	0.24	1.4	125
195	0.52	0.24	1.2	148
"	0.22	0.17	0.74	82.9
"	0.22	0.16	0.71	82.7
296	0.27	0.19	0.86	115
"	0.17	0.12	0.46	104
"	0.42	0.26	1.3	165
395	0.16	0.16	0.50	101
"	0.21	0.16	0.57	135
"	0.24	0.19	0.65	145
497	0.20	0.18	0.61	145
"	0.15	0.11	0.37	118
"	0.072	0.099	0.32	80.0

Table IV

The ratio between hydrocarbons formed in the photolysis of azoethane at different pressures and the quantum yield for formation of hydrocarbons at different pressure. Solvent 2,2,4-trimethyl pentane. Concentration of azoethane: 20 mol m^{-3}. Temperature: 22±2 °C.

Pressure /MPa		$(C_2H_6)/(C_2H_4)$	$(C_2H_4)/(C_4H_{10})$	Φ_{FH}
0.10		4.1	0.14	0.016
"		3.2	0.14	0.018
"		3.0	0.14	0.018
	Average	3.4	0.14	0.017
95		2.4	0.17	0.010
"		2.4	0.16	0.013
"		2.3	0.17	0.014
	Average	2.4	0.17	0.012
195		2.2	0.20	0.011
"		1.3	0.23	0.011
"		1.4	0.23	0.011
	Average	1.6	0.22	0.011
296		1.4	0.22	0.0095
"		1.4	0.26	0.0058
"		1.6	0.20	0.0099
	Average	1.5	0.23	0.0084
395		1.0	0.32	0.0065
"		1.3	0.28	0.0056
"		1.3	0.29	0.0060
	Average	1.2	0.30	0.0060
497		1.1	0.30	0.0055
"		1.4	0.30	0.0042
"		0.73	0.31	0.0051
	Average	1.1	0.30	0.0049

Table V

Results from the photolysis of azoethane in 2,2,4-trimethyl pentane with di-tert-butyl nitroxide as scavenger. Concentration of azoethane: 20 mol m^{-3}. Concentration of DTBN: 5.85 mol m^{-3}. Temperature: 22 ± 2 °C.

Pressure /MPa	Products formed /µmol			DTBN reacted/µmol	Quanta absorbed /µeinstein
	C_2H_6	C_2H_4	C_4H_{10}		
0.10	0.25	0.26	1.8	0.35	111
95	0.31	0.32	1.7	0.32	149
195	0.32	0.33	1.6	0.22	149
296	0.22	0.21	0.80	0.50	111
395	0.29	0.28	1.0	0.57	165
497	0.13	0.12	0.42	0.57	94.0

Table VI

The ratio between hydrocarbons formed in the photolysis of azoethane at different pressures and the quantum yields for formation of hydrocarbons and ethyl radicals at different pressures. Solvent: 2,2,4-trimethyl pentane with di-tert-butyl nitroxide as a scavenger. Concentration of azoethane: 20 mol m^{-3}. Concentration of DTBN: 5.85 mol m^{-3}. Temperature: 22 ± 2 °C.

Pressure /MPa	$(C_2H_6)/(C_2H_4)$	$(C_2H_4)/(C_4H_{10})$	ϕ_{FH}	ϕ_{FE}
0.10	0.96	0.14	0.019	0.020
95	0.97	0.19	0.014	0.015
195	0.97	0.21	0.013	0.014
296	1.1	0.26	0.0091	0.011
395	1.0	0.28	0.0078	0.0095
497	1.1	0.29	0.0058	0.0088

Results from the propionyl peroxide study

The results from the propionyl peroxide study are presented in Table VII. The amount of gas formed per hour is given in columns 2-5 and the ratios between hydrocarbons formed are provided in the next two columns. The last column lists the relative quantum yield of formation of carbon dioxide $(\phi_p)/(\phi_{P=0.1})$. The photolyses have been arranged in sets of experiments and every photolysis at a higher pressure is preceeded by a photolysis at 1 atm pressure.

It is apparent that the ratio $(C_2H_6)/(C_2H_4)$ increases with increasing pressure in contrast to the results from the photolysis of azoethane where it decreased when the pressure increased. If a scavenger was added to the solution the ratio was approximately one and unaffected by changes in pressure, as previously noted. In this study the ratio $(C_2H_4)/(C_4H_{10})$ also increases with an increase in pressure. A graphic representation of the effect of pressure on the ratio $(C_2H_4)/(C_4H_{10})$ is shown in Figure 20, plotted from the average values listed in Table VIII. The plot $\ln(k_d/k_c)$ as a function of pressure is shown in Figure 21. The calculated value of the difference in volume of activation between combination and disproportionation is 3.3 cm^3/mol.

From Table VIII it can also be seen that the relative quantum yield for formation of carbon dioxide appears to increase slightly with pressure, but since the scatter is

fairly large, as can be seen in Table VII, this may not be a real effect.

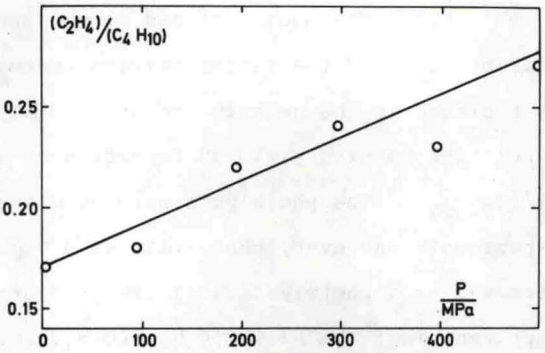


Figure 20. The ratio $(C_2H_4)/(C_4H_{10})$ as a function of pressure. Ethyl radical source: Propionyl peroxide in 2,2,4-trimethyl pentane.

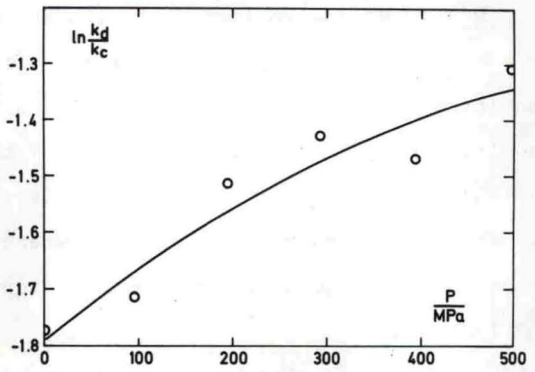


Figure 21. The effect of pressure on $\ln(k_d/k_c)$. Ethyl radical source: Propionyl peroxide in 2,2,4-trimethyl pentane.

Table VII

Results from the photolysis of propionyl peroxide in 2,2,4-trimethyl pentane at different pressures. Concentration of peroxide = 11 mol m^{-3}. Temperature: 22±2 °C.

Pressure /MPa	Products formed /μmol				$(C_2H_6)/(C_2H_4)$	$(C_2H_4)/(C_4H_{10})$	$(\phi_P)/(\phi_{0.1})$
	CO_2	C_2H_4	C_2H_6	C_4H_{10}			
0.10	12	0.70	2.5	4.6	3.6	0.15	-
0.10	14	0.72	2.4	5.0	3.3	0.14	-
0.10	12	0.68	2.5	4.4	3.7	0.16	-
0.10	15	0.78	2.8	5.0	3.6	0.16	-
95	13	0.69	3.3	3.9	4.8	0.18	0.87
0.10	19	1.0	3.4	6.7	3.4	0.15	-
95	17	0.80	4.5	4.5	5.6	0.18	0.90
0.10	17	0.84	3.0	5.2	3.6	0.16	-
95	16	0.87	4.5	4.5	5.2	0.19	0.94
0.10	18	0.94	3.4	6.2	3.6	0.15	-
95	22	1.0	5.1	6.0	5.1	0.17	1.2
0.10	16						-
195	19	1.0	6.0	4.5	6.0	0.22	1.2

Table VII continued

Pressure /MPa	Products formed /μmol				$(C_2H_6)/(C_2H_4)$	$(C_2H_4)/(C_4H_{10})$	$(\phi_P)/(\phi_{0.1})$
	CO_2	C_2H_4	C_2H_6	C_4H_{10}			
0.10	19						-
195	17	0.97	5.3	4.5	5.5	0.22	0.90
0.10	16	0.81	3.0	5.1	3.7	0.16	-
195	15	0.90	5.1	4.1	5.7	0.22	0.94
0.10	13	0.81	2.9	4.4	3.6	0.18	-
195	14	0.89	4.6	3.8	5.2	0.23	1.1
0.10	13	0.85	3.0	6.0	3.5	0.14	-
296	17	0.94	5.6	4.0	6.0	0.24	1.3
0.10	13	0.77	2.9	4.5	3.8	0.17	-
296	15	0.86	5.8	3.7	6.7	0.23	1.2
0.10	17	1.0	3.6	5.1	3.6	0.20	-
296	18	1.0	6.2	4.1	6.2	0.24	1.1
0.10	14	0.90	3.4	4.4	3.8	0.21	-
296	21	1.3	6.8	5.3	5.2	0.25	1.5
0.10	16	0.83	2.9	4.9	3.5	0.17	-
395	18	0.94	5.9	4.2	6.3	0.22	1.1

Table VII continued

Pressure /MPa	Products formed /μmol				$(C_2H_6)/(C_2H_4)$	$(C_2H_4)/(C_4H_{10})$	$(\phi_P)/(\phi_{0.1})$
	CO_2	C_2H_4	C_2H_6	C_4H_{10}			
0.10	15	0.90	3.1	4.9	3.4	0.18	-
395	16	0.98	5.3	4.0	5.4	0.25	1.1
0.10	13	0.77	2.7	4.5	3.5	0.17	-
395	16	0.96	5.9	4.2	6.2	0.23	1.2
395	17	0.98	5.8	4.3	5.9	0.23	1.3
0.10	15	0.90	3.6	5.2	4.0	0.17	-
497	13	0.84	4.8	3.5	5.7	0.24	0.87
497	16	1.1	6.1	3.7	5.6	0.30	1.1
0.10	12	0.71	2.8	3.9	3.9	0.18	-
497	19	1.2	6.9	4.1	5.8	0.29	1.6
0.10	12	0.75	2.4	4.3	3.2	0.17	-
497	13	0.69	4.7	2.8	6.8	0.25	1.1

Table VIII

The ratio between hydrocarbons at different pressures and the relative product quantum yield for formation of carbon dioxide at different pressures. Average values from Table VII.

Pressure /MPa	$(\phi_P)/(\phi_{0.1})$	$(C_2H_6)/(C_2H_4)$	$(C_3H_4)/(C_4H_{10})$
0.10	-	3.6	0.17
95	0.98	5.2	0.18
195	1.0	5.6	0.22
296	1.3	6.0	0.24
395	1.2	6.0	0.23
497	1.2	6.0	0.27

DISCUSSION

The effect of pressure on the quantum yield of decomposition of azoethane

In the determination of the quantum yield of decomposition of azoethane, the amount of ethyl radicals formed was determined rather than the amount of nitrogen formed, because of the experimental difficulties involved in the latter determination. Calculation of the quantum yield in this way requires the following assumptions:

1. Azoethane decomposes photochemically to two ethyl radicals and one molecule of nitrogen, according to the stochiometric formula

$$C_2H_5\text{-}N{=}N\text{-}C_2H_5 \xrightarrow{h\nu} 2\ C_2H_5^{\cdot} + N_2$$

2. In a system where azoethane is dissolved in 2,2,4-trimethyl pentane, and the temperature is so low that the thermal decomposition of azoethane is unimportant, ethyl radicals can only be formed from this reaction.

3. Ethyl radicals will react with each other and form the hydrocarbons ethane, ethylene and butane.

Excess of ethane over ethylene indicates abstraction of hydrogen from the solvent, forming a solvent radical which can react with a new ethyl radical and undergo either a disproportionation or combination reaction. A radical attack on the azobridge (49) according to the formula

$$C_2H_5^{\cdot} + C_2H_5\text{-}N{=}N\text{-}C_2H_5 \longrightarrow (C_2H_5)_2N\text{-}\dot{N}\text{-}C_2H_5$$

and the hydrogen abstraction reaction, which has been found in the gas phase (50)

$$C_2H_5^{\cdot} + C_2H_5\text{-}N{=}N\text{-}C_2H_5 \longrightarrow C_2H_6 + CH_3CH{=}N{=}N\text{-}C_2H_5$$

are also possible side reactions. If a scavenger is added, these side reactions are suppressed. Therefore, by choosing a scavenger whose reaction with ethyl radicals can be followed, it is possible to calculate the total amount of ethyl radicals formed and thus determine the amount of decomposed azoethane. The scavenger chosen for this system was the "stable" radical di-tert-butyl nitroxide (41), since it has no absorption in the region where azoethane absorbs and has a long wavelength absorption around 465 nm which decreases when ethyl radicals react with the nitroxide. Unfortunately the cis-form of azoethane and the product from the reaction

$$C_2H_5^{\cdot} + (t\text{-}C_4H_9)_2N\text{-}O^{\cdot} \longrightarrow (t\text{-}C_4H_9)_2NOC_2H_5$$

absorb in the same region as azoethane, i.e. around 360 nm and act as internal filters during the photolysis. This will alter the quantum yield of decomposition, but the good agreement between the value obtained in this way, ϕ=0.020 in 2,2,4-trimethyl pentane at 22 ^{o}C compared to the previous published value (16) ϕ=0.021 in hexane at 0 ^{o}C (where ϕ was determined from the amount of nitrogen formed), gives confidence in this method for determining ϕ. From

Figures 17 and 18 it is seen that the value of ϕ_{FH} increases when nitroxide has been added to the solution. This is due to a suppression of the reaction between ethyl radicals and solvent, a reaction that prevents some ethyl radicals from forming low molecular weight hydrocarbons (see below). Naturally the highest quantum yield is ϕ_{FE} which is calculated from the amount of hydrocarbons formed plus the number of nitroxide molecules reacted. The value of $\Delta V^{*} = 5.7$ cm^3/mol for decomposition of azoethane obtained from the diagram $\ln\phi = f(P)$, Figure 19, is in good agreement with values obtained from the thermal decomposition of several azo compounds (27). In this diagram the ϕ_{FE} values have been used, but the ϕ_{FH} values are superimposable on the same line.

The effect of pressure on the quantum yield of decomposition of propionyl peroxide

In the propionyl peroxide study only the relative quantum yield of formation of carbon dioxide was determined. This was made in such a way that the amount of CO_2 produced at higher pressure was compared to the amount produced at atmospheric pressure. The photolyses were performed in sets to minimize changes in the amount of light entering the cell. The absolute value of ϕ_{CO_2}, determined by Sheldon and Kochi (36), was found to be 2

and no side reactions were reported in their study. Possible side reactions would involve the attack of an ethyl radical or a propionyloxy radical on a propionyl peroxide molecule leading to a radical induced decomposition. In order to study the importance of the radical induced decomposition, a separate series of experiments was made. It was found that within the concentration range 7 mol/m^3 to 50 mol/m^3, the quantum yield was constant. At higher concentration the quantum yield increased, an indication of a radical induced decomposition. The high pressure photolyses were performed with a propionyl peroxide concentration of 11 mol/m^3 to avoid induced decomposition.

Inspection of the data presented in Table VIII reveals an increase in relative quantum yield for formation of CO_2 with increasing pressure. However, it can be seen from Table VII that because the scatter is large, the effect may not be real. Any possible explanation for an increase in the quantum yield would invariably involve a non-photochemical process since $\phi_{CO_2}=2$ naturally indicates that every excited molecule will decompose. Only if $\phi_{CO_2}<2$ could an applied hydrostatic pressure increase it, assuming that the molecules promoted to an excited state release excess energy before they decompose. Such dissipation of energy would be facilitated by an applied hydrostatic pressure, pushing the

excited molecules in closer contact with the solvent molecules, compared to at atmospheric pressure. The radical induced decomposition can be ruled out as an explanation for the high quantum yield at higher pressure, since in this study the concentration is well below the concentration region where this type of reactions occur. A dark reaction could account for the high ϕ_{CO_2}, but that no such reaction is occurring was demonstrated by checking the dark reaction at elevated pressure.

Since the increase in ϕ_{CO_2} can not be rationalized except as an experimental error, it will be assumed in the following discussion that ϕ_{CO_2} is unaffected by pressure, i.e. $\Delta V^{*} = 0$ for decomposition of propionyl peroxide.

Interpretation of the ΔV^{*} values for decomposition of azoethane and propionyl peroxide

In order to correctly interpret the values for the volume of activation it is necessary to relate them to the proper rate constants. The approach generally used for the class of compounds, which upon decomposition yields two radicals, has been to assume that in the first decomposition step, two radicals are formed in close proximity to each other in a so-called solvent cage. This approach was first used by Walling and Metzger (31) and has later been extensively used by Neuman (27). Referring to Figure 1a, the pair R-N=N$\cdot$ + R$\cdot$ should be formed with-

in such a cage.

Assuming a steady-state concentration of the cage during the photolysis, the observed rate constant for disappearance of azoethane, k_{obs}, is

$$k_{obs} = \frac{k_E k_1}{k_E + k_{-1}} \qquad [6]$$

In a system where the second step is not an elimination but a diffusive displacement (in which case k_E could be denoted k_{diff}, being much smaller than k_{-1}), the observed volume of activation is made up of three different factors

$$\Delta V^{\ddagger}_{obs} = \Delta V^{\ddagger}_1 + \Delta V^{\ddagger}_{diff} - \Delta V^{\ddagger}_{-1} \qquad [7]$$

The observed volume of activation would thus be larger than the expected activation volume for the breaking of a single bond. If equation [6] is applied to the azoethane system it can, however, be reasonable to assume that $k_E >> k_{-1}$ and the observed rate constant would be given by

$$k_{obs} = k_1 \qquad [8]$$

and the observed volume of activation

$$\Delta V^{\ddagger}_{obs} = \Delta V^{\ddagger}_1 \qquad [9]$$

Consequently, the observed volume of activation is the activation volume associated with the breaking of the C-N bond in the first decomposition step.

A conclusion that can be drawn, if the discussion above is applied to the azoethane system, is that the C_2H_5-N=N· radical has a very short life time, so short that the reverse of the first reaction step can be ignored. The low quantum yield in solution can not be explained as an effect of the solvent on the radical pair (see reference (16)) leading to a high rate of re-formation of azoethane. Evidently some other mechanism is present in the decomposition in solution. It has been suggested by Engel and Steel (19) that the decomposition in solution takes place, not in the excited molecule, but arises from thermal decomposition of the cis-isomer of azoethane. The general synthetic procedures give trans-azoethane which in solution can be photochemically converted to the cis-isomer in high yield. The cis-isomer is much less stable than the trans-isomer and decomposes to the radical products. (For a recent study of the decomposition of some cis and trans azoalkanes, see reference (51)).

By combining measurements of the temperature dependence and of the pressure dependence of the rate constant it is possible to calculate the other thermodynamic parameters for the transition state. (The necessary relations are given in most books on chemical kinetics, see for example reference (52)). Unfortunately, a complete treatment of the decomposition of azoethane is not yet

possible, since the necessary values of the activation energy and the rate constant for decomposition in solutions are not known, although values for the gas phase decomposition have been published (53). The problem is further complicated by the fact that it has not yet been unambiguously settled from which state the decomposition of azoethane occurs in solution.

Assuming that the activation volume for decomposition of propionyl peroxide is approximately zero, a different scheme emerges for its decomposition, compared to the azoethane decomposition. From the discussion of the azoethane decomposition it can be seen that any reasonable kinetic model will give a positive volume of activation of at least 4-5 cm^3/mol, i.e. the activation volume associated with the breaking of one bond in the molecule. A possible explanation for the observed activation volume follows. As suggested by Evans and Polanyi (5), ΔV^* is composed of one structural term and one solvation term. The solvation term should reflect the volume change between the transition state and the solvent. If a transition state with partial ionic character is formed, the solvation term may compensate the structural term, leading to a net volume of activation equal to zero.

This effect has been demonstrated by Hamann (54) for the hydrolysis of tert-butyl chloride. The rate determining step is

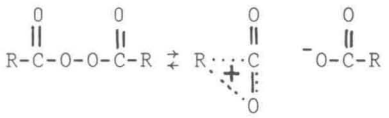
$$(CH_3)_3C\ Cl \rightarrow (CH_3)_3C^+ + Cl^-$$

followed by

$$(CH_3)_3C^+ + H_2O \rightarrow (CH_3)_3COH + H^+$$

Although this reaction is associated with the stretching and breaking of a C-Cl bond, it is accelerated by pressure, i.e. shows a negative volume of activation in that the solvation term far outweighs the structural term.

It has been proposed by Walling et al. (55) in their study of different paths in the decomposition of diacyl peroxides with secondary and tertiary alkyl groups or benzyl groups, that the decomposition goes through a transition state with a charge separation. Their model proposes the breaking of the 0-0 bond followed by formation of a transition state with charge separation



The transition state has two alternative reaction paths, one leading to common radical products, the other to the corresponding ester. The ester is not formed, however, in the photolysis of propionyl peroxide in solution, as was shown by Sheldon and Kochi (36).

If this model can be extended to include diacyl peroxides with primary alkyl groups such as propionyl peroxide, it is then possible that the transition state with

partial ionic character induces polariazation in one or more C-H bonds in the solvent. The volume decrease associated with this polarization balances the volume increase associated with the stretching of the O-O bond in the peroxide. To gain more insight into the problem of the propionyl peroxide decomposition it is necessary to study, in addition to the studies by Smid et al. (56) on the solvent dependence of the rate constant, the pressure effect on the rate constant in different solvents. This would make it possible to calculate other activation parameters for the decomposition.

In light of the above, some remarks can be made as to the concerted versus nonconcerted decomposition of these compounds. It seems reasonable to assume that azoethane decomposes by a nonconcerted mechanism followed by a fast nitrogen elimination. However, it is possible to state a priori, that azoethane decomposes by a two-bond scission with ΔV^* for breaking two C-N bonds equal to 5.7 cm^3/mol. Owens and Koenig (57) have suggested that in the comparison of ΔV^* values for decomposition, it is best to differentiate between reversibility and non-reversibility of the dissociation step rather than between different mechanisms involving different transition states. Following this suggestion, it can be concluded that azoethane decomposes with negligible re-formation of the parent molecule. For the per-

oxide the mechanism is complex and can not be explained in terms of simultaneous breaking of one or more bonds. However, it is reasonable to assume that the re-formation of the parent molecule is negligible.

Disproportionation-combination reactions of ethyl radicals

The cross reactions between two alkyl radicals are shown in Figure 1c. As previously noted, if it is assumed that ethylene and butane are formed only from these cross reactions, the plot of $\ln k_d/k_c$ versus P will give the difference in volume of activation between the two reaction paths. The ΔV^* values presented in the section Results are in reasonably good agreement with each other. The value from the second azoethane study is higher than both the values from the first azoethane study and the propionyl peroxide study. This difference could be interpreted as a temperature effect (the photolyses in the first azoethane study were performed at 35 ^{o}C and in the second azoethane study at 22 ^{o}C), if not the results from the propionyl peroxide study gave $\Delta V^* = 3.3$ cm^3/mol compared to the value 4.4 cm^3/mol from the second azoethane study. Since activation volumes generally can not be determined with an accuracy better than ± 1 cm^3 it is assumed that these data are within the experimental accuracy and the value of $\Delta V^* = 4.0$ cm^3/mol is given as an average value from the different studies in 2,2,4-

trimethyl pentane. The value from the photolysis of azoethane in toluene is compatible with this value.

The results presented above are written as a difference in volume for the activated complex leading to combination and to disproportionation ($\Delta V_c^* - \Delta V_d^*$). In solution the reactions between ethyl radicals are diffusion controlled and should be retarded by an applied hydrostatic pressure (1). However, it is reasonable to assume that both reactions have a negative volume of activation, i.e are accelerated by an applied pressure, once the ethyl radicals are sufficiently close together that a reaction is possible. Since the ratio k_d/k_c increases with pressure, evidently ΔV^* for combination is less negative than ΔV^* for disproportionation.

The value of the difference in ΔV^* may appear small. However, it should be noted that the ΔV^* for breaking of a C-O or C-N bond is approximately 5 cm^3/mol and that the value for formation of a C-C bond is roughly the same, but with different sign. Thus, the difference in volume of activation is remarkably large and can only be accounted for by a very pronounced difference in the structures of the two transition states. It should also be noted that these measurements can not distinguish between a common transition state and two different transition states, although the large difference in ΔV^*

favours the two transition state theory. However, the difference in volume of activation can be interpreted according to the Kerr and Trotman-Dickenson model (25), assuming that the common transition state has two alternative ways to decompose, of which the one leading to formation of ethane and ethylene requires the least volume.

As can be seen from the diagrams of $\ln k_d/k_c = f(P)$ there is a decrease in curvature at the higher pressures, but since there is a large scatter in data this flattening can not readily be quantified to a difference in ΔV^* at higher pressure. Moreover, since an adequate theory of the pressure dependence on the volume of activation is lacking, it is sufficient to note that a decrease in ΔV^* with pressure is interpreted as a higher compressibility of the transition state than that of the reacting species. In the case with the two competing reactions between the ethyl radicals, since the difference in volume of activation is decreasing, the activated complex leading to combination is more compressible than the complex leading to disproportionation.

The reactions of ethyl radicals with solvent and scavenger

Ethyl radicals formed in solution have a certain probability to react with the solvent molecules. In an aliphatic solvent this reaction is initiated by a hydrogen abstraction

$$C_2H_5^{\cdot} + SH \rightarrow C_2H_6 + S^{\cdot}$$

The radical derived from the solvent, $S^{\cdot}$, can then react with an ethyl radical or another radical derived from the solvent or perhaps attack a solvent molecule and abstract a hydrogen atom. Since ethane is formed in the first step of the reaction between an ethyl radical and a solvent molecule, and since the disproportionation between the ethyl radicals yields equal amounts of ethane and ethylene, the excess of ethane over ethylene serves as a quantitative measure of the ethyl radicals which have reacted with the solvent.

By the addition of a scavenger for the ethyl radicals, the above reactions can be suppressed, by the scavenging of those radicals diffusing in the solution. The addition of a scavenger will also prevent the radical induced decomposition of the precursor.

In the first azoethane study, where 1,1-diphenyl ethylene was added as a scavenger, it can be seen from Tables I and II that the ratio $(C_2H_6)/(C_2H_4)$ is close to unity. This indicates that almost all ethyl radicals which diffuse away from their original partners are trapped by the scavenger. The trapping mechanism involves the addition of the ethyl radical to the vinyl group.

In the second azoethane study, di-tert-butyl nitroxide was used as a scavenger (see Table VI). The nitroxide is evidently a very efficient scavenger for ethyl radicals

since the ratio $(C_2H_6)/(C_2H_4)$ is equal to one. The reaction between a molecule of DTBN and an ethyl radical is one of a simple addition (as noted above) producing an ethoxy amine.

The different behaviour of the $(C_2H_6)/(C_2H_4)$ ratios in absence of scavenger with an applied pressure in the second azoethane study and in the propionyl peroxide study presents an interesting problem. As previously noted, ethane can be formed by the disproportionation or by abstraction of hydrogen from the solvent. It is reasonable to assume that since the abstraction proceeds via a stretching of a C-H bond, it should have a positive volume of activation, i.e. be retarded by an applied pressure. This effect is observed in the second azoethane study, see Figure 22. However, the reverse effect is observed in the propionyl peroxide study, Figure 23, which can perhaps be ascribed to the difference between the source of the ethyl radicals.

One apparent difference that can be noted when comparing the ethyl radicals formed from the peroxide and those from azoethane, is the distance difference in the two ethyl radicals formed. To take an extreme case, if two ethyl radicals are formed from the dissociation of butane, the cross reaction between the two radicals should be more probable than a diffusional migration of the radicals leading to a subsequent hydrogen abstraction.

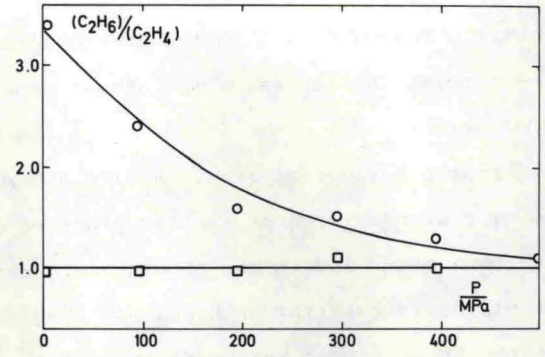


Figure 22. The ratio $(C_2H_6)/(C_2H_4)$ as a function of pressure.
□ Azoethane in 2,2,4-trimethyl pentane with di-tert-butyl nitroxide.
○ Azoethane in 2,2,4-trimethyl pentane.

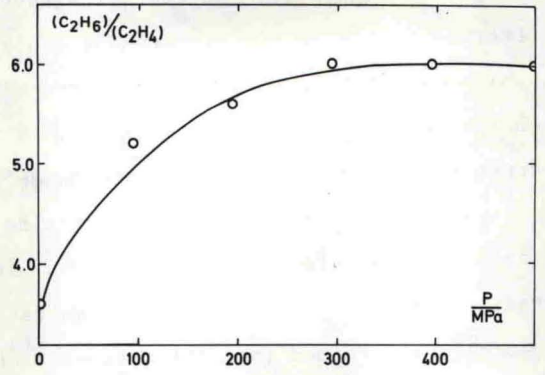


Figure 23. The ratio $(C_2H_6)/(C_2H_4)$ as a function of pressure. Ethyl radical source: Propionyl peroxide in 2,2,4-trimethyl pentane.

Generally, the closer the radicals are formed to one another the higher the probability for recombination. Since the $(C_2H_6)/(C_2H_4)$ ratios at atmospheric pressure are approximately equal in the two studies, being 3.4 in the azoethane study and 3.6 in the propionyl peroxide study, it is evident that the ethyl radicals have an almost equal probability to diffuse apart, regardless of the radical source. Furthermore, the fact that the radicals are formed at different distance from each other can not explain the difference in the pressure effect on the $(C_2H_6)/(C_2H_4)$ ratio. Upon an increase in pressure the rotation and diffusion of the species will decrease (2,58,59) and the result will be a general slow-down of the molecular motion. The reactions will be affected in such a way that a reaction with a high positive ΔV^* should be less probable than a reaction with a small ΔV^*. This is probably the explanation for the observed decrease in the $(C_2H_6)/(C_2H_4)$ ratio in the azoethane study. Since a similar effect is not observed in the propionyl peroxide system, one must conclude that either some specific effect, associated with the transition state of the decomposing peroxide, or some other reaction with a negative ΔV^* leads to an increase in the rate of formation of ethane with increasing pressure.

A radical induced decomposition could have a negative volume of activation, as shown by Nicholson and Norrish

(29) in their study of the decomposition of benzoyl peroxide, but such an induced decomposition would probably proceed by abstraction of a hydrogen atom from the peroxide and yield equal amounts of ethane and ethylene. As previously noted, no dark reaction has been found in this study, but it is possible that a careful examination of other products that may be formed in this system can solve this problem.

In addition to a recent study by Pratt (60), the reaction between NO and ethyl radicals has been studied in which the prominent steps are the addition reaction

$$C_2H_5^{\cdot} + NO \rightarrow C_2H_5NO$$

followed by the dimerization of nitrosoethane to the trans-dimer. It was found that an addition of NO (c = = 1 mol/m^3) to the propionyl peroxide solution removed all ethyl radicals and led to the formation of no new low molecular weight hydrocarbons. The amount of CO_2 formed was roughly the same as in the experiments without scavenger. This indicates that none of the ethyl radical pairs undergo a cage reaction but diffuse in the solution before a reaction is possible. This reaction can occur, unless a scavenger is present, with ethyl radicals derived from the same propionyl peroxide molecule or with ethyl radicals derived from different molecules.

The reactions between the ethyl radicals and solvent

are probably the reason for the poor material balance in the propionyl peroxide study. When the peroxide decomposes, $n_{CO_2} = n_{C_2H_5}$, i.e. the number of CO_2 molecules formed is the same as the number of ethyl radicals formed. If ethyl radicals could form only butane, ethane or ethylene the material balance should be

$$n_{CO_2} = (n_{C_2H_6} + n_{C_2H_4} + 2\, n_{C_4H_{10}})$$

There remains, however, the possibility that ethyl radicals disappear through reaction with solvent radicals rendering the number of ethyl radicals less than that of low molecular weight hydrocarbons.

SUMMARY

Two compounds, azoethane and propionyl peroxide, have been photolyzed in solution in the pressure region 0.1 MPa to 500 MPa and the effect of pressure on the quantum yield for decomposition studied. The quantum yield for decomposition of azoethane decreased with an applied pressure, giving a positive value for the volume of activation while the quantum yield for decomposition of propionyl peroxide was unaffected by pressure within the experimental limits. This has been interpreted as a decomposition of azoethane by scission of a C-N bond, followed by a fast nitrogen elimination and as a decomposition of propionyl peroxide proceeding via a transition state with partial ionic character.

The pressure effect on the competing reactions of the ethyl radicals has also been studied and the difference in volume of activation between combination and disproportionation has been determined. The large value obtained for the difference indicates that these reactions proceed via two different transition states.

The reactions between ethyl radicals and the solvent, 2,2,4-trimethyl pentane, have also been studied. The hydrogen abstraction reaction of the ethyl radicals was found to decrease with pressure when the radical source was azoethane and increase when the radical source was the peroxide.

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REFERENCES

1. Weale, K.E., Chemical Reactions at High Pressures. E. & F.N. Spon Ltd., London, 1967.
2. Hamann, S.D., Physico-Chemical Effects of Pressure. Butterworths scientific publications, London, 1957.
3. Eckert, C.A., Ann. Rev. Phys. Chem. 1972, 23, 239.
4. Kohnstam, G., Progr. React. Kinet. 1970, 5, 335.
5. Evans, M.G. and Polanyi, M., Trans. Faraday Soc. 1935, 31, 875.
6. Koenig, T., in Free Radicals (ed. J.K. Kochi), Vol. I. John Wiley & Sons, New York, 1973.
7. Cubbon, R.C.P., Progr. React. Kinet. 1970, 5, 29.
8. Strausz, O.P., Lown, J.W. and Gunning, H.E., in Comprehensive Chemical Kinetics (ed. C.H. Bamford and C.F.H. Tipper), Vol. 5. Elsevier Publishing Company, Amsterdam, 1972.
9. Herk, L., Feld, M. and Szwarc, M., J. Am. Chem. Soc. 1961, 83, 2998.
10. Bawn, C.E.H. and Halford, R.G., Trans. Faraday Soc. 1955, 51, 780.
11. Braun, W., Rajbenbach, L. and Eirich, F.R., J. Phys. Chem. 1962, 66, 1591.
12. Janzen, E.G. and Blackburn, B.J., J. Am. Chem. Soc. 1968, 90, 5909.
13. Perkins, M.J., in Essays on Free-radical Chemistry. The Chemical Society, London, 1970.

14. Hammond, G.S. and Soffer, L.M., J. Am. Chem. Soc. 1950, 72, 4711.

15. Crawford, R.J. and Takagi, K., J. Am. Chem. Soc. 1972, 94, 7406.

16. Kodama, S., Fujita, S., Takeishi, J. and Toyama, O., Bull. Chem. Soc. Jpn. 1966, 39, 1009.

17. Bevington, J.C., Proc. R. Soc. London, Ser. A 1957, 239, 420.

18. Bevington, J.C. and Lewis, T.D., Trans. Faraday Soc. 1958, 54, 1340.

19. Engel, P.S. and Steel, C., Acc. Chem. Res. 1973, 6, 275.

20. Franck, J. and Rabinowitsch, E., Trans. Faraday Soc. 1934, 30, 120.

21. Noyes, R.M., Progr. React. Kinet. 1961, 1, 129.

22. Eisenthal, K.B., Acc. Chem. Res. 1975, 8, 118.

23. Ward, H.B., in Free Radicals (ed. J.K. Kochi), Vol. I. John Wiley & Sons, New York, 1973.

24. Gibian, M.J. and Corley, C., Chem. Rev. 1973, 73, 441.

25. Kerr, J.A. and Trotman-Dickenson, A.F., Progr. React. Kinet. 1961, 1, 105.

26. Benson. S.W., Advan. Photochem. 1964, 2, 1.

27. Neuman Jr., R.C., Acc. Chem. Res. 1972, 5, 381.

28. Walling, C. and Pellon, J., J. Am. Chem. Soc. 1957, 79, 4782.

29. Nicholson, A.E. and Norrish, R.G.W., Disc. Faraday Soc. 1956, 22, 97.

30. Ewald, A.H., Disc. Faraday Soc. 1956, 22, 138.

31. Walling, C. and Metzger, G., J. Am. Chem. Soc. 1959, 81, 5365.

32. Vogt Jr., T.C.and Hamill, W.H., J. Phys. Chem. 1963, 67, 292.

33. Nicholson, A.E. and Norrish, R.G.W., Disc. Faraday Soc. 1956, 22, 104.

34. Tanaka, F., Sasaki, M. and Osugi, J., Nippon Kagaku Zasshi 1971, 92, 883. (C.A. 1972, 76, 24376x.)

35. Dixon, P.S., Stefani, A.P. and Szwarc, M., J. Am. Chem. Soc. 1963, 85, 2551.

36. Sheldon, R.A. and Kochi, J.K., J. Am. Chem. Soc. 1970, 92, 4395.

37. Neuman Jr., R.C., J. Org. Chem. 1972, 37, 495.

38. Backman, C.-M., Claesson, S. and Szwarc, M., Trans. Faraday Soc. 1970, 66, 3061.

39. Kochi, J.K. and Mocadlo, P.E., J. Org. Chem. 1965, 30, 1134.

40. Wagner, C.D., Smith, R.H. and Peters, E.D., Anal. Chem. 1947, 19, 976.

41. Hoffman, A.K., Feldman, A.M., Gelblum, E. and Hodgson, W.G., J. Am. Chem. Soc. 1964, 86, 639.

42. Hatchard, C.G. and Parker, C.A., Proc. R. Soc. London, Ser. A 1956, 235, 518.

43. Kasha, M., J. Opt. Soc. Am. 1948, 38, 929.

44. Claesson, S., Malmrud, S. and Lundgren, B., Trans. Faraday Soc. 1970, 66, 3048.

45. Andersson, G.R., Arkiv Kemi 1963, 20, 513.

46. Claesson, S., Lundgren, B. and Szwarc, M., Trans. Faraday Soc. 1970, 66, 3053.

47. Dietz, W.A., J. Gas Chromatog. 1967, 5, 68.

48. Bridgman, P.W., Proc. Am. Acad. Arts Sci. 1931, 67, 1.

49. Wan, J.K.S., Hess, L.D. and Pitts Jr., J.N., J. Am. Chem. Soc. 1964, 86, 2069.

50. Strausz, O.P., Berkley, R.E. and Gunning, H.E., Can. J. Chem. 1969, 47, 3470.

51. Engel, P.S. and Bishop, D.J., J. Am. Chem. Soc. 1975, 97, 6754.

52. Laidler, K.J., Chemical Kinetics, McGraw-Hill, New York, 1965.

53. Sandhu, H.S., J. Phys. Chem. 1968, 72, 1857.

54. Buchanan, J. and Hamann, S.D., Trans. Faraday Soc. 1953, 49, 1425.

55. Walling, C., Waits, H.P., Milovanovic, J. and Pappiannou, C.G., J. Am. Chem. Soc. 1970, 92, 4927.

56. Smid, J., Rembaum, A. and Szwarc, M., J. Am. Chem. Soc. 1956, 78, 3315.

57. Owens, J. and Koenig, T., J. Org. Chem. 1974, 39, 3153.

58. Barton, A.F.M. and Speedy, R.J., High Temp. High Pressures 1970, 2, 587.

59. Claesson, S. and Jones, D.R., Chemica Scripta 1976, in press.

60. Pratt, G. and Veltman, I., J. Chem. Soc., Faraday Trans. 1, 1974, 70, 1840.