## Discussion

The results reported above suggest strongly that the decomposition of diacetyl peroxide is a unimolecular reaction, and the work of Kharasch and his school implies that we measure the rate of the unimolecular dissociation

$$CH_3{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}CH_3 \longrightarrow 2CH_3{\cdot}CO_2 \qquad (1)$$

The present work adds the following evidence in favor of this assumption:

1. Some methane *is* produced in the decomposition and its quantity is consistent with the assumption that it results from reactions which involve methyl radicals. This observation indicates that ethane is *not* produced by a direct decomposition of diacetyl peroxide according to equation 4

$$CH_3{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}CH_3 \longrightarrow C_2H_6 + 2CO_2 \qquad (4)$$

but by the recombination of methyl (or perhaps acetate) radicals.

2. It seems that the same reaction initiates the thermal decomposition of diacetyl peroxide in gas phase and in solution, since the rate of decomposition and the activation energy are essentially the same in both phases (see the following paper). On the other hand, there is no doubt that the decomposition in solution involves radicals.

We may conclude, therefore, that the observed activation energy represents the O–O bond dissociation energy in diacetyl peroxide, *i.e.*

$$D(CH_3{\cdot}CO{\cdot}O\text{–}O{\cdot}CO{\cdot}CH_3) = 29.5 \text{ kcal./mole}$$

From this value one may calculate the heat of formation of acetate radical

$$\Delta H_f(CH_3{\cdot}CO_2) = {}^1/_2\{29.5 + \Delta H_f\,(CH_3{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}CH_3)\}$$

and subsequently, the related bond dissociation energies, like $D(CH_3{\cdot}COO\text{–}H)$. At present the heat of formation of diacetyl peroxide is not known, but we hope that it will be determined in the near future.

In conclusion, we would like to thank the National Science Foundation and the Research Corporation for the financial support of this work.

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[CONTRIBUTION FROM THE COLLEGE OF FORESTRY, STATE UNIVERSITY OF NEW YORK]

# Kinetics of the Thermal Decomposition of Diacetyl Peroxide. II. Effects of Solvents on the Rate of the Decomposition

BY M. LEVY, M. STEINBERG AND M. SZWARC

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The kinetics of the thermal decomposition of diacetyl peroxide has been studied in 9 solvents in the temperature range 55–85°. In sufficiently dilute solutions (*i.e.*, less than 0.1 *M*), the decomposition is essentially first order. At higher concentrations the induced second-order reaction begins to be significant, and it has been shown that the latter reaction is caused mainly by the solvent radicals. The comparison of the decomposition carried out in solutions with that taking place in the gaseous phase suggests that some recombination $2CH_3COO \rightarrow (CH_3COO)_2$ takes place in the "cage." This cage recombination probably is responsible for the observed changes in the apparent activation energy of the process.

In the present communication we shall try to elucidate the influence of a solvent on the rate and on the activation energy of the decomposition of acetyl peroxide. The kinetics of this decomposition has been studied in the temperature range 55–85° in the following solvents: isoöctane, cyclohexane, benzene, toluene, glacial acetic acid, propionic acid and in three fluorochemicals.

## Experimental

The method of preparation of diacetyl peroxide is described in part I of this series. Crystals of the peroxide were dissolved in the required solvent and its concentration was determined by the iodometric titration method described by Wagner, Smith and Peters.[1] The solvents were acquired commercially. Isoöctane was of "spectroscopically pure" grade, benzene, toluene and acetic acid were of "analytically pure" grade, while propionic acid was of "chemically pure" grade. Three fluorochemicals were used, namely: a cyclic ether corresponding probably to a formula $CF_3{\cdot}C_5F_9O$ manufactured by Minnesota Mining Co. (Trade name Fluorochemical 0-75), fluorinated methylcyclohexane ($CF_3{\cdot}C_6F_{11}$) manufactured by Columbia Organic Chemicals Co., and fluorinated dimethylcyclohexane $(CF_3)_2{\cdot}C_6F_{10}$, manufactured by du Pont Co. (denoted as FCX 327). The solvents were distilled before use, and it was shown that all but fluorochemicals do not contain any peroxides.[2]

The following procedure was adopted in most experiments. Five cc. of the peroxide solution followed by 5 cc. of the pure solvent was pipetted into a 30-cc. flask provided with a constriction and an inner ground joint. The flask was attached to a high vacuum line, its contents frozen by immersing it into a solid carbon dioxide–acetone bath, and then evacuated until a vacuum of about $10^{-5}$ mm. was attained. Thereafter the contents of the flask were thawed, and then the freezing and evacuation procedure repeated for two more times. After the third evacuation the flask was sealed off at the constriction and immersed into a constant temperature bath. The temperature of the bath was kept constant within a limit better than ±0.1°, and the reading of the thermometer was compared with the reading of a precision thermometer calibrated by The National Bureau of Standards.

After a predetermined period of time (2–64 hours),[3] the flask was removed from the bath, cooled in a solid carbon dioxide–acetone bath, opened, and the contents analyzed for the undecomposed peroxide. The experimental results, expressed in the form of first-order rate constants are listed in Table I.

Some experiments were carried out in an apparatus from which aliquots of the solution could be withdrawn without admitting air to the reaction chamber.

## Results

The first-order kinetics of the decomposition of diacetyl peroxide was confirmed by two methods. Using the apparatus mentioned previously the fraction of decomposition *f* was determined as a

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

[2] We found that 10 cc. of $CF_3{\cdot}C_6F_{11}$ liberates 0.75 × $10^{-2}$ millimole of iodine, 10 cc. of FCX 327 liberates 1 × $10^{-2}$, and 10 cc. of 0–75 liberates 4.1 × $10^{-2}$ millimole of iodine.

[3] It was shown that the contents of the flask attain the temperature of the bath within 5 minutes.

TABLE I

DECOMPOSITION OF DIACETYL PEROXIDE

| Solvent | $T$, °C. | $M \times 10^3$ | No. of expt. | Av. $k \times 10^5$, sec.$^{-1}$ | Mean square dev., % |
|---|---|---|---|---|---|
| Isoöctane | 55.2 | 9.5 | 2 | 0.235 | ±1.2 |
| Isoöctane | 55.2 | 93.0 | 2 | 0.270 | ±0.8 |
| Isoöctane | 64.9 | 3.9 | 2 | 0.92 | ±0.4 |
| Isoöctane | 64.9 | 7.7 | 8 | 0.94 | ±0.9 |
| Isoöctane | 64.9 | 80.0 | 9 | 1.08 | ±1.2 |
| Isoöctane | 75.2 | 9.4 | 5 | 4.03 | ±0.8 |
| Isoöctane | 75.2 | 92.0 | 4 | 3.90 | ±3.7 |
| Isoöctane | 85.2 | 8.6 | 2 | 14.9 | ±0.1 |
| Isoöctane | 85.2 | 88.5 | 2 | 15.6 | ±0.3 |
| Cyclohexane | 55.2 | 6.0 | 4 | 0.21 | ±5.3 |
| Cyclohexane | 55.2 | 60.0 | 2 | 0.23 | ±0.0 |
| Cyclohexane | 55.2 | 99.5 | 2 | 0.23 | ±0.0 |
| Cyclohexane | 64.9 | 3.2 | 6 | 0.83 | ±0.9 |
| Cyclohexane | 64.9 | 8.0 | 6 | 0.88 | ±1.5 |
| Cyclohexane | 64.9 | 11.8 | 2 | 0.88 | ±0.5 |
| Cyclohexane | 64.9 | 29.5 | 6 | 0.92 | ±1.5 |
| Cyclohexane | 64.9 | 75.8 | 7 | 0.97 | ±1.2 |
| Cyclohexane | 75.2 | 5.3 | 5 | 3.60 | ±1.2 |
| Cyclohexane | 75.2 | 60.0 | 2 | 3.80 | ±3.1 |
| Cyclohexane | 75.2 | 102.5 | 4 | 3.85 | ±3.1 |
| Cyclohexane | 85.2 | 5.4 | 2 | 12.7 | ±0.6 |
| Cyclohexane | 85.2 | 97.0 | 2 | 14.5 | ±1.3 |
| Benzene | 55.2 | 8.8 | 2 | 0.26 | ±1.0 |
| Benzene | 55.2 | 86.0 | 1 | 0.29 | . . . |
| Benzene | 64.9 | 8.7 | 12 | 1.07 | ±1.4 |
| Benzene | 64.9 | 86.5 | 12 | 1.11 | ±1.5 |
| Benzene | 75.2 | 9.2 | 4 | 4.65 | ±2.7 |
| Benzene | 75.2 | 84.0 | 5 | 4.05 | ±5.8 |
| Benzene | 85.2 | 9.2 | 4 | 16.2 | ±1.2 |
| Benzene | 85.2 | 96.0 | 4 | 17.5 | ±0.2 |
| Toluene | 55.2 | 6.85 | 2 | 0.27 | ±0.3 |
| Toluene | 55.2 | 68.5 | 1 | 0.28 | . . . |
| Toluene | 64.9 | 6.85 | 4 | 1.14 | ±0.6 |
| Toluene | 64.9 | 68.5 | 3 | 1.18 | ±1.1 |
| Toluene | 75.2 | 6.85 | 4 | 4.70 | ±0.3 |
| Toluene | 75.2 | 68.5 | 4 | 4.80 | ±0.4 |
| Toluene | 85.2 | 6.85 | 3 | 15.9 | ±1.5 |
| Toluene | 85.2 | 68.5 | 4 | 15.4 | ±0.5 |
| Acetic acid | 55.2 | 10.0 | 2 | 0.28 | ±0.0 |
| Acetic acid | 55.2 | 91.1 | 2 | 0.22? | ±1.1 |
| Acetic acid | 64.9 | 10.0 | 3 | 0.99 | ±2.5 |
| Acetic acid | 64.9 | 91.1 | 4 | 0.90 | ±0 8 |
| Acetic acid | 75.2 | 10.0 | 4 | 3.75 | ±1.9 |
| Acetic acid | 75.2 | 91.1 | 3 | 3.50 | ±1.7 |
| Acetic acid | 85.2 | 10.0 | 2 | 13.0 | ±1.0 |
| Acetic acid | 85.2 | 46.5 | 2 | 12.8 | ±0.2 |
| Acetic acid | 85.2 | 91.1 | 2 | 12.3 | ±0.5 |
| Propionic acid | 64.9 | 15 | 2 | 1.4 | . . . |
| Propionic acid | 85.2 | 15 | 2 | 16.6 | . . . |
| Propionic acid | 85.2 | 57 | 2 | 15.9 | . . . |

function of time. The negative values of ln $(1 - f)$ were plotted against time and yielded straight lines. Furthermore, the experiments in which the initial concentration of the peroxide was varied lead to values for the first-order rate constants which are essentially independent of the concentration of the peroxide (see Table I).

The decomposition of acetyl peroxide in perfluorochemicals solutions proceeds about half as rapidly as in other solvents listed in Table II. These experiments were often irreproducible and, therefore, the results are omitted from Table I.

The first-order rate constant has been determined for 4 temperatures, namely, 55.2, 64.9, 75.2 and 85.2°. The plots of logarithms of $k$ against reciprocals of temperature yield excellent straight lines and the computed activation energies are listed in Table II. The latter entities are calculated on the basis of results obtained in diluted solutions (*i.e.*, 8 or 9 × $10^{-3}$ $M$). For the sake of comparison the data obtained by other investigators are included in Table II. On the whole the agreement between the various workers is very satisfactory.

TABLE II

| Solvent | $k$ for 85.2°, sec.$^{-1}$ × $10^5$ | $E$, kcal./mole | Ref. |
|---|---|---|---|
| Gas phase | 22.4 | 29.5 | Part I |
| Acetic acid | 13.0 | 30.2 | This paper |
| Acetic acid | 11.8 | ? | Ref. 5 |
| Propionic acid | 16.6 | ? | This paper |
| Isoöctane | 14.9 | 32.2 | This paper |
| Cyclohexane | 12.7 | 31.4 | This paper |
| Benzene | 16.2 | 32.3 | This paper |
| Toluene | 15.9 | 32.0 | This paper |
| Toluene | 14.1 | 31.0 | Ref. 4 |
| Toluene | 16.3 | 33.0 | Ref. 5 |
| Carbon tetrachloride | 11.7 | 33.4 | Ref. 7 |
| Carbon tetrachloride | 9.9 | ? | Ref. 5 |

The decomposition of diacetyl peroxide in a toluene solution was investigated by Walker and Wild[4] and by Ross and Fineman.[5] In both these investigations about 0.05 $M$ solutions of the peroxide were used and the kinetics of the decomposition was shown to be first order from the behavior of individual runs. In our study the initial concentration of the peroxide was varied by a factor of 10, from 0.007 to 0.07 $M$, and it was found that such a variation in concentration has a negligible effect on the rate constant, leading to its increase by 2–4%, only. Inspection of Table II shows that the agreement between our data and those of Walker and Wild, and of Ross and Fineman is very good.

Ross and Fineman studied also the kinetics of decomposition of acetyl peroxide in acetic acid solution at 73.2°. They showed that the first-order character of the reaction is preserved even if the decomposition exceeds 90%, and that the first order-rate constant is independent of the concentration of the peroxide in the range of 0.05–0.5 $M$. On the other hand, our data seem to indicate that the reaction is slightly inhibited at higher concentrations of the peroxide, namely, a 5–10% decrease in the first-order rate constant is observed when the initial concentration of the peroxide is increased from 0.01 to 0.1 $M$.[6] Nevertheless, the agreement between our data and those of Ross and Fineman is satisfactory.

The kinetics of decomposition of acetyl peroxide in carbon tetrachloride was investigated by Ed-

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[4] O. J. Walker and G. L. Wild, *J. Chem. Soc.*, 1132 (1937).

[5] S. D. Ross and M. A. Fineman, THIS JOURNAL, **73**, 2176 (1951).

[6] The same observation has been made in a solution of propionic acid.

wards and Mayo,[7] and by Ross and Fineman.[5] The latter workers claim that the first-order rate constant of the decomposition proceeding in this solvent increases by 30% when the concentration of the peroxide is increased tenfold, from 0.05 to 0.5 *M*, and assume that this phenomenon is due to the induced decomposition. It seems to us, however, that a re-examination of the decomposition proceeding in the latter solvent would be desirable since, according to Edwards and Mayo, presence of a small amount of acetic anhydride is essential to ensure the reproducibility of results.

No data are reported in the literature on the kinetics of decomposition of acetyl peroxide in other solvents. Our present work shows that this reaction is essentially first order in isoöctane, cyclohexane, benzene and propionic acid, although a tenfold increase in the concentration of the peroxide increases the first-order rate constant by 5–15% in isoöctane solution, 10–15% in cyclohexane solution, and 4–10% in benzene solution. Probably the induced decomposition is responsible for this deviation from the first-order kinetics, nevertheless, it appears that the rate constants measured at low concentrations of the peroxide (*i.e.*, below 0.01 *M*) represent the "true" first-order rate constants.

It is significant that the effect of concentration is negligible in toluene solutions. This observation seems to point out that the induced decomposition is caused primarily by the solvent radicals, and thus its extent varies from solvent to solvent according to the reactivity of the R radicals (RH denotes the molecule of a solvent).

The comparison of the rates and the activation energies of the decomposition in solution and in the gaseous phase is particularly interesting. Inspection of Table II shows that the rate constants of the decomposition in the solvents listed in Table II are numerically very similar and, furthermore, they all are lower than the rate constant found for the gaseous reaction.[8] We suggest the following interpretation for these observations. In the gaseous phase an activated molecule of the peroxide decomposes in an irreversible way. The chance that the fragments produced by the decomposition would recombine and regenerate the molecule of peroxide is extremely small. On the other hand, since the decomposition in a solution takes place in a cage,[9] it is conceivable to expect a relatively high value for the probability of recombination. Thus, if the recombination of the fragments is the *only* cause for the difference in the rates of the reaction in a solution and in the gaseous phase, our result would indicate that the probability of recombination at 85.2° is 0.27 in toluene solution and 0.43 in cyclohexane solution. Furthermore, we would expect an increase in this probability with decreasing temperature of the reaction, and retaining the above assumptions, we calculate the probability of recombination in toluene solution at 55° at 0.38. In this interpretation the increasing probability of recombination with decreasing temperature accounts for the increase in the activation energy of the decomposition.

The above interpretation can be expressed in slightly different language. The activation energy for the gaseous decomposition is equal to the amount of energy required for the rupture of the O–O bond. The same amount of energy is necessary to rupture the O–O bond in solution; however, fragments endowed with a higher energy have a greater chance to escape from the cage. Consequently the *apparent* activation energy in solution would be higher than that observed for the gaseous reaction, and the difference between these activation energies should be similar in magnitude to the activation energy of the diffusion process.

It should not be concluded from the above discussion that the recombination in a cage represents the *only* interaction between the solvent molecules and those of the decomposed peroxide. The partition function of a peroxide molecule in the gaseous phase is very different from that of a molecule in solution. It seems, however, that in the present case the ratio $f^{\ddagger}/f_{\text{init.}}$ is affected only slightly by the surroundings. It is particularly illuminating to discuss at this juncture the differences in the activation energies in the gaseous phase and in solutions. For example, the activation energy for the decomposition in toluene solution is higher by about 2.5 kcal./mole from that observed for the gaseous reaction. One might argue that this difference represents an increase in the height of the potential energy barrier, caused, *e.g.*, by the work performed on pushing apart molecules of solvent. Such a suggestion, although attractive, seems to be improbable. An increase of 2.5 kcal./mole in the activation energy calls for a 30-fold decrease in the rate of the reaction, while the rate decreases by a factor of 1.4 only. It would be surprising if the gain in the entropy of activation would balance so closely the decrease in the rate due to the increase in the activation energy. Furthermore, *would* the above suggestion be correct, one should expect an increase in the activation energy of the process with increasing cohesive energy of the solvent. Such a relation is not brought out by the observations.

The solvents discussed above seem to be inert toward acetyl peroxide. However, there are solvents which do interact with acetyl peroxide and appreciably affect the rate of decomposition. For example, we observed a strong acceleration of the reaction by pyridine, quinoline, acetic anhydride and so forth.[10] These phenomena call for further investigation, which we hope to carry out in the future.

Finally, let us consider the effects of solvents on the rates of other reactions involving a homolytic fission of a chemical bond. The decomposition of di-*t*-butyl peroxide was studied in the gaseous phase and in solutions. It was found by Raley, Rust and Vaughan[11] that the rates of the de-

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[7] F. G. Edwards and F. R. Mayo, This Journal, **72**, 1265 (1950).

[8] Table II lists the data for 85.2°. However, these observations are equally valid for data obtained at lower temperatures (*e.g.*, at 55°).

[9] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[10] Similar effects were observed in the decomposition of benzoyl peroxide; see, for example, Bartlett and Nozaki, This Journal, **69**, 2299 (1947).

[11] J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 1336 (1948).

composition are essentially the same in both phases, and that a change of solvent only slightly affects the rate of the decomposition. The rate of the primary decomposition of the following compounds was found to be affected only slightly by the nature of an inert solvent: benzoyl peroxide,[12] *t*-butyl perbenzoate,[13] and hexaphenylethane[14] (the latter reaction was investigated in 28 solvents). Unfortunately, neither of these reactions were studied in gaseous phase.

Recently, Alder and Leffler[15] investigated the effect of solvents on the rate of homolytic dissociation of phenylazotriphenylmethane. Analysis of their data shows again that the rates of the decomposition are only slightly affected by the nature of a solvent, although the apparent activation varies by about 4.5 kcal./mole. The approximate constancy of the rate constants demands a linear relation between activation energy and entropy of activation, and therefore it is not surprising that such a relation was found by the latter authors.

In conclusion, we would like to thank the National Science Foundation for financial support of this investigation.

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[12] P. D. Bartlett and K. Nozaki, THIS JOURNAL, **68**, 1686 (1946); C. G. Swain, W. Stockmayer and T. Clarke, *ibid.*, **72**, 5426 (1950); C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

[13] A. T. Blomquist, THIS JOURNAL, **73**, 3408, 3412, 5546 (1951).

[14] K. Ziegler, P. Orth and K. Weber, *Ann.*, **504**, 131 (1933).

[15] M. G. Alder and J. E. Leffler, THIS JOURNAL, **76**, 1425 (1954).

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# The Kinetics of Decomposition of Acetyl Peroxide. III. The Reactions of Radicals Produced in the Decomposition

BY M. LEVY AND M. SZWARC

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A technique has been developed for determining quantitatively small amounts of methane, ethane and carbon dioxide produced in the thermal decomposition of dilute solutions of acetyl peroxide. It seems that in a diluted solution of isooctane or cyclohexane methyl radicals are converted quantitatively into methane and ethane, the latter being probably produced in a cage reaction. On the other hand, a considerable fraction of methyl radicals is "lost" in benzene solution, and it was shown that such a "loss" is due to the direct addition of methyl radicals to an aromatic molecule. Such a reaction seems to be characteristic for an aromatic compounds–radicals interaction. There is evidence that acetate radicals are more stable in solution of acetic acid or propionic acid than in solution of hydrocarbons. It is suggested that this increase in the stability is due to hydrogen bonding between the radical and the solvent. Finally, the decomposition has been studied in solution of fluorochemicals in a vain attempt to find a solvent which would be inert toward radicals.

This communication, denoted at Part III of the present series, is devoted to a discussion of elementary reactions involving the radicals produced by the thermal decomposition of diacetyl peroxide, and is based on experiments in which the rates of formation of carbon dioxide, methane and ethane were measured.

## Experimental

Thoroughly evacuated solutions of acetyl peroxide (10 cc.) were sealed in a flask provided with a break seal. The flask was immersed in a heating bath, the temperature of which was kept constant within ±0.1°. At the end of a predetermined period of time, the flask was removed, its contents frozen immediately, and then analyzed with help of an apparatus shown schematically in Fig. 1. The reaction flask R is attached to a ground joint linked with trap $T_1$. The latter was cooled to $-115°$ using frozen ethyl bromide as a cooling agent. The whole apparatus was evacuated below $10^{-5}$ mm. Thereafter, the break seal was broken with the help of a magnetic hammer (M), and the contents of the flask were distilled over to Trap $T_1$. During the distillation, the two pumps (a mercury vapor pump and a Toepler pump) were simultaneously operating and consequently carbon dioxide, methane and ethane produced in the reaction were transferred to trap $T_2$ and storage section S. Blank runs have shown that this procedure enables one to separate quantitatively all these gases from the solvent.

Trap $T_2$ was cooled by liquid nitrogen, and thus the carbon dioxide and the ethane remained frozen. Therefore, the pressure in the system measured the amount of methane produced in the reaction. When the latter was determined, the liquid nitrogen bath was replaced by a solid carbon dioxide–acetone bath, and the increase in pressure measured, then the amount of $CO_2 + C_2H_6$ produced. Finally, the amount of $CO_2$ produced was measured by absorbing the latter by ascarite.

## Results and Discussion

The experimental results are listed in Tables I, II and III. Inspection of these tables brings out the following points. For the decomposition, carried out in a diluted isoöctane or in cyclohexane solution at 65°, the ratio $(CH_4 + 2C_2H_6)/CO_2$ is unity within experimental error. This indicates that under these experimental conditions neither reaction (1) nor (2) takes place to any measurable extent.

$$CH_3{\cdot}COO + CH_3 \longrightarrow CH_3{\cdot}COOCH_3 \qquad (1)$$

$$CH_3 + (CH_3COO)_2 \longrightarrow CH_3{\cdot}COOCH_3 + CH_3{\cdot}CO_2 \qquad (2)$$

TABLE I

DECOMPOSITION OF ACETYL PEROXIDE IN ISOÖCTANE[a]

| *T*, °C. | *M* × 10³ | Time, hr. | No. exper. | $\frac{2CO_2}{\text{peroxide decomp.}}$ | $\frac{CH_4}{CO_2}$ | $\frac{C_2H_6}{CO_2}$ | $\frac{CH_4 + 2C_2H_6}{CO_2}$ |
|---|---|---|---|---|---|---|---|
| 64.9 | 9.5 | 1 | 1 | 1.05 | 0.776 | 0.115 | 1.005 |
| 64.9 | 9.5 | 2 | 8 | 0.95 | .817 | .077 | 0.971 |
| 64.9 | 9.5 | 4 | 2 | .95 | .873 | .058 | .989 |
| 64.9 | 9.5 | 8 | 1 | .98 | .770 | .023 | .816(?) |
| 64.9 | 9.5 | 16 | 1 | .82(?) | .840 | .079 | .998 |
| 64.9 | 9.5 | 32 | 1 | .92 | .800 | .033 | .866(?) |
| 64.9 | 94 | 1 | 1 | .85 | .805 | .036 | .877 |
| 64.9 | 94 | 2 | 1 | .83 | .817 | .035 | .887 |
| 85.2 | 6 | 2 | 3 | .86 | .815 | .045 | 905 |
| 85.2 | 11 | 2 | 2 | .87 | .790 | .048 | .886 |

[a] The values quoted in the last four columns represent average values if more than one experiment was performed.