

statistics require at least two different chemical species of  $C_6H_{12}^+$  ions that have different label retentions and contribute disproportionately to each of the secondary decomposition products. The requirement could be met by ethylcyclobutane and propylcyclopropane intermediates arising from 1,4- and 1,3-elimination, respectively. In consequence of the differences in geometry and in ring strain, propylcyclopropane ion would be expected to yield a different distribution of products of further breakdown than ethylcyclobutane. The difference in strain energy between the cyclobutyl and cyclopropyl rings is only about 2 kcal./mole,<sup>26,27</sup> exceedingly small beside the energy of the impinging electrons. However, similarly small differences between ring-strain energies in methylcyclopentane and methylcyclohexane and between dissociation energies of the alkyl-cycloalkyl bonds in methyl- and ethylcyclopentanes have been found to exert marked influence on relative rates of competing reactions leading to isomeric products.<sup>19</sup>

Multiple processes involving isomeric ions cannot be fully disentangled; details are not entirely clear. Even so, considerable specificity is evident in hexanol decomposition—especially in the primary loss of  $H_2O$ , but also, though to a lesser extent, in secondary reactions.<sup>28</sup>

### Experimental

The hexanols were prepared by reaction of unlabeled and appropriately labeled 1-bromopropanes with trimethylene oxide,<sup>29</sup>

(26) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(27) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, p. 26.

(28) As this communication was being prepared to go to press, we learned of pertinent results reported by K. Biemann to the Welch Foundation Conference on Modern Developments in Analytical Chemistry, in Houston, Texas, Nov., 1963. In the respective mass spectra of butanol-2- $d_2$ , pentanol-3- $d_2$ , hexanol-4- $d_2$ , and heptanol-5- $d_2$  < 1, 3, 90, and 5% of the water lost from parent ions contained a deuterium atom—in essential agreement with our findings.

(29) S. Searles, *J. Am. Chem. Soc.*, **73**, 124 (1951).

which in turn was prepared from 3-chloropropanol<sup>30</sup> (27.5% yield).

To prepare unlabeled hexanol, 5.8 g. (0.1 mole) of trimethylene oxide was added with stirring to the Grignard reagent prepared from 12.3 g. (0.1 mole) of 1-bromopropane and 2.4 g. (0.1 g.-atom) of magnesium in 75 ml. of anhydrous ether. The reaction mixture was heated under reflux on a steam bath for 1 hr., 50 ml. of dry benzene was added, and the ether was distilled off. The benzene solution was then heated for 4 hr. on a steam bath, cooled, and poured into 50 ml. of ice-cold dilute hydrochloric acid. The benzene layer was separated and the aqueous solution was extracted with pentane. Evaporation of the organic solvents gave a pale yellow oil which was a mixture of hexanol and 3-bromopropanol. The crude product was added to a solution of 5.0 g. of potassium hydroxide in 10 ml. of methanol and 2 ml. of water and heated for 2 hr. under reflux on a steam bath. After cooling, the solution was poured into water and the oily layer was taken up in pentane. Evaporation of the pentane left an oil which was purified by distillation on a vacuum line at ambient temperature and 0.05 torr pressure. The 3.1 g. (31% yield) of hexanol so obtained was colorless and gave a negative Beilstein test.

Hexanol-4- $d_2$ , -5- $d_2$ , and -6- $d_3$  were prepared similarly from 5.0 g. (0.04 mole) of 1-bromopropane-1- $d_2$ , -2- $d_2$ , and -3- $d_3$ , respectively, purchased from Merck Sharp and Dohme, Montreal, Canada. Yields were all about 35%.

Chemical purities (weight %) of the hexanols, estimated by gas chromatography, were: unlabeled, 92.5; -4- $d_2$ , 84.5; -5- $d_2$ , 90.3; -6- $d_3$ , 90.8. Final purification by gas chromatography gave fractions, the mass spectra of which revealed no impurities. The labeled 1-bromopropanes were stated by the vendor to have minimum isotopic purities of 98 atom %. Mass spectra of the hexanols do not permit precise isotopic analysis; however, they suggest that isotopic purity is in every case close to 100 atom %.

Mass spectra were measured with 70-v. electrons on a modified<sup>31</sup> Consolidated Model 21-103c instrument with the inlet system at 250°. Low-voltage measurements were made with the repeller plates at an average potential of 3 v.; actual settings, adjusted for maximum ion current, were 4.00 v. on the inner repeller and 2.00 v. on the outer one.

**Acknowledgment.**—We are grateful to D. K. Albert for assistance with gas chromatography.

(30) C. R. Noller, *Org. Syn.*, **29**, 92 (1949).

(31) H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Moller, 7th Annual Meeting of ASTM Committee E-14 on Mass Spectrometry, Los Angeles, Calif., 1959.

[CONTRIBUTION NO. 7990 FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL OF CANADA, OTTAWA, CANADA]

## The Mercury-Photosensitized Decomposition of Propane at Temperatures above 300°

BY R. A. BACK AND S. TAKAMUKU<sup>1</sup>

RECEIVED JANUARY 31, 1964

A reinvestigation of the mercury-photosensitized decomposition of propane at temperatures from 300 to 400° has yielded results very similar to those obtained earlier by Bywater and Steacie, despite considerably improved conditions for kinetic measurements. It appears likely that an approximate equilibrium was established between *n*-propyl and isopropyl radicals. The resultant low concentrations of *n*-propyl radicals (3 to 6%) probably account for the abnormally low rate of formation of methane, which arose largely *via* the decomposition of *n*-propyl rather than isopropyl radicals. Rate constants for this decomposition, based on calculated values of [*n*-propyl], are in fair agreement at 300° with values obtained by extrapolation of the data of Calvert and Slepoy obtained at lower temperatures, but with rising temperature fall well below these values.

### Introduction

Some of the earliest estimates of bond-dissociation energies in alkyl radicals come from studies of the mercury-photosensitized decomposition of alkanes at

elevated temperatures. It has since become evident that some of these estimates are considerably lower than the correct values,<sup>2</sup> although the reason for this has never been clearly explained. About 12 years ago,

(1) National Research Council of Canada Postdoctorate Fellow, 1961-1962.

(2) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 107 (1961).

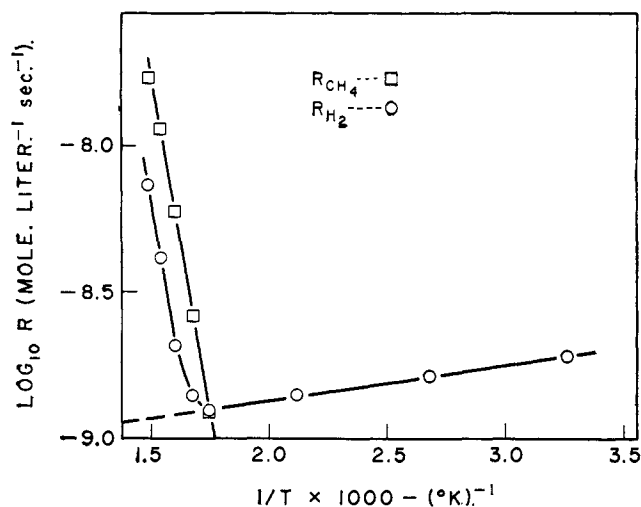
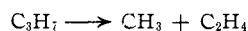


Fig. 1.—Arrhenius plot of the rates of production of methane and hydrogen.

in this laboratory, Bywater and Steacie derived values of about 20 and 38 kcal./mole, respectively, for the activation energies of the reactions



from the high-temperature (300–450°) mercury-photosensitized decomposition of propane.<sup>3</sup> More recent experimental estimates of  $E$  for the first reaction above range between 25 and 35 kcal./mole for the  $n$ -propyl and from 30 to 33 for the isopropyl radical,<sup>2,4–7</sup> with the higher values generally favored, although none of the data is entirely convincing. Recent estimates of  $E$  for the second reaction, on the other hand, are in close agreement with the earlier one of Bywater and Steacie.<sup>2–7</sup>

In conjunction with another problem, we have recently reinvestigated briefly the mercury-photosensitized decomposition of propane at temperatures up to 400°, under conditions rather simpler and better suited to kinetic measurements than those of the earlier work. The present paper describes the results of these experiments.

### Experimental

The irradiation system has been described previously.<sup>8</sup> The 200-cc. cylindrical reaction vessel was incorporated in an efficient circulating system of about 3500-cc. volume. Methane and hydrogen, the only products measured, were removed through a suitable train of traps by a Toepler pump and measured in a gas buret. Hydrogen was then removed by diffusion through hot palladium at 300° and the residual methane measured. This method of analysis agreed well with mass spectrometric measurements which also showed that methane and hydrogen were the only noncondensable products.

The pressure of propane (Phillips research grade) was about 300 mm. in all experiments. The concentration of olefin impurities in this propane was known from previous experiments to be low enough that loss of hydrogen atoms by addition reactions was negligible. Mercury vapor in the system was at the equilibrium vapor pressure at 0°, and absorbed a fraction of the 2537 Å. resonance radiation which depended on both temperature and

(3) S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 319 (1951).

(4) J. G. Calvert and W. C. Sleppy, *J. Am. Chem. Soc.*, **81**, 1544 (1959).

(5) J. A. Kerr and J. G. Calvert, *ibid.*, **83**, 3391 (1961).

(6) J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **55**, 572, 921 (1959).

(7) W. M. Jackson and J. R. McNesby, *J. Am. Chem. Soc.*, **83**, 4891 (1961); *J. Chem. Phys.*, **36**, 2272 (1962).

(8) R. A. Back and D. van der Auwera, *Can. J. Chem.*, **40**, 2339 (1962).

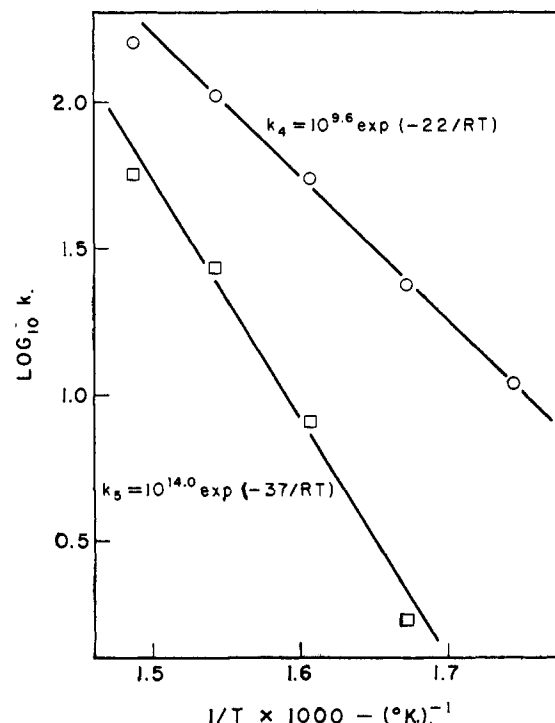


Fig. 2.—Arrhenius plot of values of  $k_4$  and  $k_5$  based on total propyl radical concentration, assuming  $k_3 = 10^{11}$  mole<sup>-1</sup> l. sec.<sup>-1</sup>.

propane pressure, presumably through line-broadening effects. In the experiments of interest for propyl radical decomposition between 300 and 400°, the absorption was about 60%. While this absorption was still far from homogeneous throughout the reaction vessel, any effect of inhomogeneous absorption should have been very much less than in the earlier work of Bywater and Steacie,<sup>3</sup> in which, it has been suggested,<sup>2</sup> such effects may have led to serious errors.

Per cent conversion in all experiments was low enough so that true initial yields of H<sub>2</sub> and CH<sub>4</sub> were measured, and addition of H or CH<sub>3</sub> to propylene produced in the reaction was negligible.<sup>9</sup>

### Results

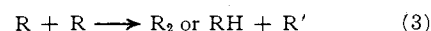
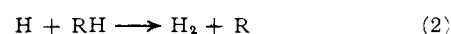
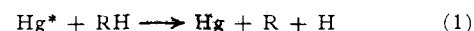
Table I summarizes the experimental results, while Fig. 1 shows a simple Arrhenius plot of  $R_{\text{CH}_4}$  and  $R_{\text{H}_2}$ .

TABLE I

Temp., °C.	$R_{\text{H}_2}$	$R_{\text{CH}_4}$	$R_1$	$R_{\text{H}_2(\text{chain})}$	[R], moles/l. × 10 <sup>10</sup>	$k_4$	$k_5$
33	1.88	...	1.88	...	1.37	...	...
100	1.62	...	1.62	...	1.27	...	...
200	1.42	...	1.42	...	1.19	...	...
300	1.23	1.21	1.23	...	1.11	10.9	...
325	1.41	2.61	1.22	0.19	1.10	23.7	1.7
350	2.08	5.96	1.20	0.88	1.09	54.7	8.1
375	4.11	11.38	1.17	2.94	1.08	105	27.2
400	7.29	17.02	1.16	6.13	1.08	158	56.8

### Discussion

At temperatures below about 300° in the present system, the following simple mechanism is well established<sup>9</sup>



where RH = propane and R' = propylene. Under the present conditions of low conversion and low light intensity, no other reactions occur, and  $R_{\text{H}_2} = R_2 = R_1$ .

(9) R. A. Back, *ibid.*, **37**, 1834 (1959).

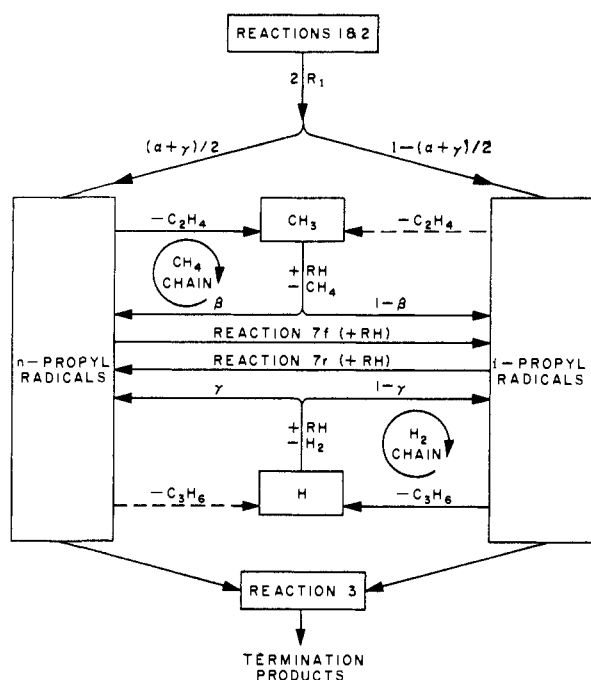
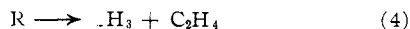
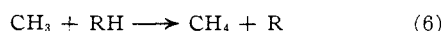


Fig. 3.—Interrelations between *n*-propyl and isopropyl radicals in the mercury-photosensitized decomposition of propane.

It is also quite well established that the methane and additional hydrogen produced as the temperature is raised comes from decomposition of propyl radicals<sup>3</sup>



followed by

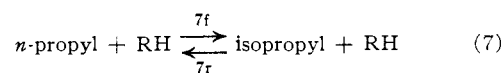


and reaction 2. The reaction pairs 4 and 6, and 5 and 2, constitute reaction chains producing methane and hydrogen without a net consumption of propyl radicals. If then  $R_1$  and  $R_3$  are approximately independent of temperature, simple Arrhenius plots of  $R_{CH_4}$  and  $R_{H_2} - R_1$  should yield activation energies for reactions 4 and 5. In the present system a small correction was made for the slow decrease in  $R_{H_2}$  with increasing temperature evident in Fig. 1 at low temperatures, which was shown to be due to decreasing absorption of the 2537 Å. resonance radiation. Values for  $R_1$ , the nonchain rate of production of hydrogen, were evaluated from Fig. 1 by an extrapolation of the linear decrease; these and values of  $R_{H_2(\text{chain})}$  are shown in Table I. Also shown in Table I are absolute values of  $k_4$  and  $k_5$  derived by assuming  $[R] = (R_1/k_3)^{1/2}$  and  $k_3 = 10^{11}$  mole<sup>-1</sup> l. sec.<sup>-1</sup>. From Arrhenius plots of these values, shown in Fig. 2, the relations  $k_4 = 10^{9.6} \exp(-22/RT)$  sec.<sup>-1</sup> and  $k_5 = 10^{14.0} \exp(-37/RT)$  sec.<sup>-1</sup> were obtained.

These activation energies are in good agreement with the values of 20 and 38 kcal./mole obtained from essentially similar plots by Bywater and Steacie,<sup>3</sup> despite several notable differences in the experimental conditions. First, in the earlier work, an appreciable fraction of the propyl radicals was formed by the addition of hydrogen atoms to propylene, and it might be suggested that vibrational excitation of radicals thus formed might account for an abnormally low activation energy for decomposition. This complication was

avoided in the present work, and the close agreement with Bywater and Steacie suggests that this effect was unimportant in both systems. Second, the absorbed light intensity was about one-thirtieth as high in the present work. This favors first-order decomposition of radicals over the second-order combination reactions and causes decomposition to set in at lower temperatures. The Arrhenius plots in Fig. 1 are parallel to those of Bywater and Steacie, but shifted to temperatures about 50° lower. Finally, the absorption of light in the present system was much more homogeneous, as discussed previously. Despite these considerable differences in experimental conditions, very similar values of  $E_4$  and  $E_5$  were obtained in the two systems.

Both the activation energy and frequency factor found for reaction 5 are in good agreement with recent measurements.<sup>2-7</sup> For reaction 4, both Arrhenius parameters are too low, although  $E_4$  is in fair agreement with the value of 25.2 found for *n*-propyl radicals by Kerr and Trotman-Dickenson<sup>6</sup> which has, however, been questioned.<sup>5,7</sup> The absolute values of  $k_4$  in Table I are obviously much too low.<sup>2-7</sup> Estimates of  $k_4$  in the present system are complicated by the fact that both *n*-propyl and isopropyl radicals were present. It is well known that *n*-propyl decomposes by reaction 4 much faster than does isopropyl, and in fact it may be shown that to a first approximation all the methane formed in the present experiments came from decomposition of *n*-propyl radicals.<sup>7</sup> Thus in evaluating  $k_4$ , the concentration of *n*-propyl, rather than the total radical concentration, should be employed. Several factors govern the *n*-propyl concentration: (a) the ratio of *n*-propyl/isopropyl formed in reaction 1; (b) the ratio of *n*-propyl/isopropyl formed in the abstraction reactions 2 and 6; (c) the relative rates of decomposition of *n*-propyl and isopropyl in reactions 4 and 5; (d) the relative rates of removal of *n*-propyl and isopropyl in the combination reaction (3); and (e) the efficiency of the equilibration reactions



The interrelation of these factors is illustrated in Fig. 3, from which an expression for the steady-state concentration of *n*-propyl radicals may be derived.

$$[n\text{-}C_3H_7] = \frac{(\alpha + \gamma)R_1 - (1 - \beta)R_{CH_4} + \gamma R_{H_2(\text{chain})} + [R][RH]k_{7f}}{[RH](k_{7f} + k_{7r}) + 2[R]k_3}$$

in which  $[R]$  represents the total radical concentration, and  $\alpha$ ,  $\beta$ , and  $\gamma$  are the fractions of *n*-propyl radicals formed in reactions 1, 6, and 2, respectively. Inherent in this expression are two simplifying assumptions: (a) all  $CH_4$  arose by decomposition of *n*-propyl radicals; (b) all chain hydrogen arose from decomposition of isopropyl radicals; in other words, loss of isopropyl by reaction 4 and of *n*-propyl by reaction 5 was negligible. Calculations based on reported values of  $k_4$  and  $k_5$  show that errors introduced by these assumptions are small and in opposite directions, tending to cancel. A value of  $\alpha = 0.42$  was assumed.<sup>10</sup> Values of  $\beta$  were

(10) G. N. C. Woodall and H. E. Gunning, *Bull. soc. chim. Belges*, **71**, 725 (1962).

calculated from estimates of the rates of reaction of  $\text{CH}_3$  with primary and secondary hydrogen,<sup>2</sup> from which

$$\begin{aligned} \beta/(1 - \beta) &= (6 \times 10^{8.3} \exp(-10.4/RT))/2 \times \\ & \quad 10^{8.0} \exp(-8.3/RT) \\ &= 6 \exp(-2.1/RT) \end{aligned}$$

Values of  $\gamma$  were estimated from the relation

$$\gamma/(1 - \gamma) = 6 \exp(-1.0/RT)$$

Hydrogen atoms should be considerably less selective than  $\text{CH}_3$ ; the reduction of  $\Delta E$  from 2.1 to 1.0 kcal. is a crude attempt to take this into account.

It was further assumed in deriving the expression for [*n*-propyl] that  $R_3 = k_3([\textit{n}-propyl] + [\textit{i}sopropyl])<sup>2</sup> so that [*n*-propyl] + [\textit{i}sopropyl] =  $(R_1/k_3)^{1/2} = [R]$ . This requires that reactions 2 and 6 were fast enough so that concentrations of  $\text{CH}_3$  and H were always negligible compared to propyl. Values of  $[\text{CH}_3]$  were calculated from the relation  $[\text{CH}_3] = R_{\text{CH}_3}/k_6[\text{RH}]$ , taking  $k_6 = 6 \times 10^{8.3} \exp(-10.4/RT) + 2 \times 10^{8.0} \exp(-8.3/RT)$ ,<sup>2</sup> and were found to be always less than 0.5% of the total radical concentration. Concentrations of hydrogen atoms should have been even lower since reaction 2 is much faster than reaction 6.$

Two sets of values of  $k_{7f}$  were calculated from the relations  $k_{7f} = 10^8 \exp(-10/RT)$  and  $k_{7f} = 10^8 \exp(-11/RT)$ . Values of  $k_{7r}$  were derived from  $k_{7f}$  and the equilibrium constant  $K_7$ , which was taken as  $\exp((4.0/RT) - 0.25)$ .<sup>2,7,11</sup>

Table II shows values of  $\beta$ ,  $\gamma$ ,  $K_7$ , and  $k_{7f}$ . Values of [*n*-propyl] were calculated, based on five sets of conditions, and are shown in Table III as percentages of the total radical concentration.

TABLE II

Temp., °C.	$\beta$	$\gamma$	$K_7$	$-k_{7f}$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>	
				$E_{7f} = 10$	$E_{7f} = 11$
33	0.16	0.54	580	6.8	1.3
100	0.26	0.61	176	133	34
200	0.39	0.67	58	2300	787
300	0.48	0.71	27	$1.47 \times 10^4$	6170
325	0.50	0.72	23	$2.15 \times 10^4$	9100
350	0.52	0.73	20	$2.98 \times 10^4$	$1.33 \times 10^4$
375	0.54	0.73	18	$4.10 \times 10^4$	$1.85 \times 10^4$
400	0.55	0.74	16	$5.50 \times 10^4$	$2.6 \times 10^4$

TABLE III

Temp., °C.	CALCULATED VALUES OF [ <i>n</i> -PROPYL] (%)				
	Equilibrium between <i>n</i> -C <sub>3</sub> H <sub>7</sub> and <i>i</i> -C <sub>3</sub> H <sub>7</sub>	$\gamma$ from Table II	$\gamma$ from		
			$E_{7f} = 10$ , Table 11	$E_{7f} = 11$ , Table 11	$E_{7f} = 11$ , $\gamma = \beta$
33	0.17	48.1	46.4	47.9	28.8
100	0.56	52.4	31.1	44.4	29.1
200	1.70	55.0	6.52	13.7	7.92
300	3.57	31.3	4.03	4.73	4.26
325	4.16	9.09	4.23	4.30	3.94
350	4.76	-34.6	4.40	3.98	3.62
375	5.26	-72.9	4.75	4.10	3.60
400	5.88	-74.4	5.48	5.00	4.35

The negative values of [*n*-propyl] obtained in column 3 show that the equilibration reactions cannot be neglected. Indeed, it seems unlikely that  $E_{7f}$  is greater than 10 kcal.<sup>10,12</sup> and it is evident from

(11) W. M. D. Bryant, *J. Polymer Sci.*, **6**, 359 (1951).

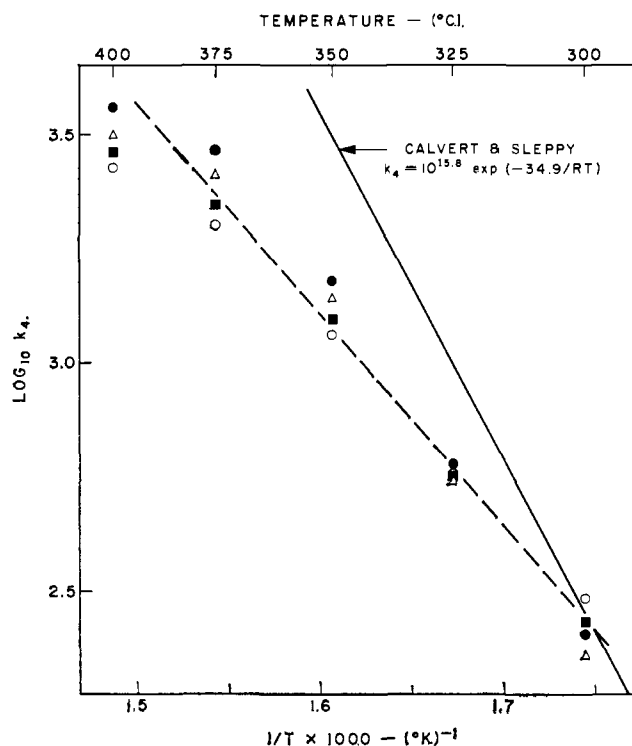


Fig. 4.—Arrhenius plots of  $k_4$  based on calculated concentrations of *n*-propyl radicals taken from Table III: O, equilibrium;  $\Delta$ ,  $E_{7f} = 10$ ,  $\gamma$  from Table II;  $\square$ ,  $E_{7f} = 11$ ,  $\gamma$  from Table II;  $\bullet$ ,  $E_{7f} = 11$ ,  $\gamma = \beta$ .

Table III that [*n*-propyl] is probably not far from its equilibrium value between 300 and 400°. This would also offer a simple explanation of the agreement between the present results and those of Bywater and Steacie, since if the radicals were equilibrated, the differences in experimental conditions noted earlier would be unimportant.

Calculated values of [*n*-propyl] between 300 and 400° for  $E_{7f} = 11$  kcal. show a downward trend up to 350°, but turn upward again at higher temperature; of the calculated values none shows the systematic decrease in [*n*-propyl] with rising temperature which could account for a low value of  $E_1$ . Values of  $k_4$  derived from the calculated *n*-propyl concentrations are plotted in Fig. 4 and are seen now to be in fair agreement with the high-pressure data of Calvert and Sleppy<sup>4</sup> at 300°, but to fall below an extrapolation of their data at higher temperatures. This behavior parallels that of the data of Kerr and Trotman-Dickenson when compared with that of Kerr and Calvert, both at lower pressures.<sup>5</sup> The broken line in Fig. 4 corresponds to  $E_4 = 22$  kcal.

Our conclusions may be briefly summarized:

(1) It seems probable that in the high-temperature (300–450°) mercury-photosensitized decompositions of propane, isopropyl and *n*-propyl radicals are approximately in equilibrium, so that the mode of formation of radicals—whether in the primary step, by abstraction, or by addition to propylene—is unimportant. Equilibrium at these temperatures corresponds to *n*-propyl concentrations between 3 and 6% of the total

(12) Woodall and Gunning found hexanes corresponding to about 5% *n*-propyl in the mercury-photosensitized decomposition of propane at room temperature. This suggests that the equilibration reaction was quite efficient even at this temperature, since at least 25% of the radicals formed should have been *n*-propyl, so that  $E_{7f}$  may be considerably less than 10 kcal.

radical concentration. If then  $\text{CH}_4$  comes largely from decomposition of *n*-propyl, and chain hydrogen from the decomposition of isopropyl, both the very low values of  $k_4$  and the normal values of  $k_5$ , obtained by calculations based on the total radical concentration, are explained.

(2) The corrected values for  $k_4$  appear to support the observation of Kerr and Trotman-Dickenson that

at temperatures above  $300^\circ$   $k_4$  falls well below an extrapolation of data obtained at lower temperatures, leading to an apparently lower value of  $E_4$ . It seems unlikely that the true value of  $E_4$  is as low as 22 or 25 kcal., and the low values observed probably arise from a systematic decline in the pre-exponential term with rising temperature. Speculation as to the cause of such behavior is not warranted here.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNSYLVANIA]

## The Heats of Combustion of Aliphatic Long Chain Peroxyacids, *t*-Butyl Peroxyesters, and Related Acids and Esters<sup>1</sup>

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RECEIVED JANUARY 29, 1964

The heats of combustion of peroxyauric, peroxyauristic, peroxyaurpalmitic, and peroxyaurstearic acids, myristic, palmitic, and stearic acids, *t*-butyl peroxyaurcaprate, peroxyauraurate, and peroxyaurmyristate, and *t*-butyl caprylate, caprate, laurate, and myristate have been measured. By use of values or estimates of values of the heats of fusion and vaporization, the results have been converted to the  $25^\circ$  standard-state heats of combustion for the gaseous substances for all the peroxyesters and esters and for peroxyaurauric acid. The application of the thermochemical group additivity rule to the heats of formation of organic peroxides has been examined. A higher order approximation to the general law of disproportionations may be needed for some of the peroxides. Calculated dissociation energies of *t*-butyl peroxyauraurate and peroxyaurauric acid are compared with enthalpies of activation observed for the free radical decompositions of these substances.

### Introduction

The understanding of many of the properties of organic peroxides will be aided greatly by the thermodynamic information that can be obtained by direct calorimetric determination of the heats of combustion of those substances. Unfortunately, such determinations have been generally impractical owing to the instability and lack of purity of the peroxides so that, for the great part, less direct means have been used to estimate those thermodynamic quantities.

Recently, improved methods have been obtained<sup>3-5</sup> for the preparation of long chain aliphatic peroxyacids and *t*-butyl peroxyesters in pure form. With these highly purified, relatively stable substances available, it has been possible to determine for the first time their heats of combustion. In order to obtain auxiliary data for the calculation of the heats of some other reactions, the heats of combustion of the parent fatty acids and their *t*-butyl esters have also been measured.

### Experimental

**Materials.**—The long chain fatty acids used in the combustion measurements and as starting materials for the preparation of the esters, peroxyacids, and peroxyesters were obtained from the Eastman Kodak Co. and, after fractional distillation at 4–7 mm., samples converted to their methyl esters were examined for homologs by gas-liquid chromatography. Methyl esters of several of the acids were also fractionated. No homologs or other impurities were present in any case.

The fatty acids whose heats of combustion were to be determined were then treated by recrystallization procedures designed to convert them into their C forms.<sup>6</sup> The final identification and

estimation of the polymorphic forms present was always carried out after pelletizing the acid. The third- and fifth-order long spacings<sup>6</sup> on the Cu  $K\alpha$  X-ray diffraction powder photographs were measured for this purpose.

Stearic acid was recrystallized successfully from olefin-free, dry, freshly-distilled petroleum ether at room temperature and then kept at  $50^\circ$  for 48 hr. to eliminate completely all traces of the A form.<sup>6</sup> Palmitic acid was converted satisfactorily by recrystallization from acetic acid. Myristic acid was recrystallized from its own pure melt and also from acetic acid. In the case of lauric acid, neither the recrystallization from the melt nor that from various solvents at different temperatures gave reproducible polymorph content and, furthermore, the content changed on standing. Similar difficulty with lauric acid is indicated in studies made by Davies and Malpass.<sup>7</sup>

The peroxyacids were prepared from the fatty acids by the method of Parker and co-workers<sup>3</sup> and Silbert and co-workers.<sup>5</sup> The peroxy oxygen content of these compounds determined by iodometric titration<sup>3,5</sup> was between 99.4 and 100.5% of theoretical, with half of the batches having values in the range 99.9 to 100.1%. Pelletizing had no effect on the peroxy oxygen content. The long spacing of the peroxyaurpalmitic acid, 37.2 Å., was the same as found by Swern and co-workers.<sup>8</sup> It was unaffected by pelletizing. No evidence for polymorphism within the even-carbon peroxyacid series below 18 carbon atoms has been noted to date, although recent evidence suggests a polymorphic difference between the odd and even series.<sup>9</sup> Only the even carbon members are considered in this investigation.

Both the *t*-butyl esters and the *t*-butyl peroxyesters were prepared by pyridine acylation methods.<sup>4,10</sup> The esters after fractional distillation *in vacuo* showed no impurities in gas-liquid chromatography. The peroxyesters were purified by passage through silica gel and elution with petroleum ether containing 4 to 5% of diethyl ether, the best fractions being chosen by iodometric titration.<sup>11</sup> The peroxy oxygen content of the final prod-

(1) A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Eastern Utilization Research and Development Division of the Agricultural Research Service. Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

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