Thermal Decomposition of Some TertButyl Compounds at Elevated Temperatures

Wing Tsang

Citation: The Journal of Chemical Physics **40**, 1498 (1964); doi: 10.1063/1.1725353
View online: http://dx.doi.org/10.1063/1.1725353
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/40/6?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 40, NUMBER 6 15 MARCH 1964

Thermal Decomposition of Some *Tert*-Butyl Compounds at Elevated Temperatures

WING TSANG
National Bureau of Standards, Washington, D. C. 20234

(Received 15 October 1963)

A single-pulse shock tube has been used to study the kinetics of the thermal decomposition of *tert*-butyl chloride, bromide, alcohol, and mercaptan. The results are compared with those obtained by earlier workers who used static reaction vessels at lower temperatures. The rate constants for the unimolecular elimination reactions are

$$k_{\mathrm{C_4H_9Cl}}=10^{13.9}e^{-46\,200/RT}\qquad(750°\text{–}950°\mathrm{K}),$$

$$k_{\mathrm{C_4H_9Br}}=10^{13.5}e^{-41\,500/RT}\qquad(700°\text{–}900°\mathrm{K}),$$

$$k_{\mathrm{C_4H_9OH}}=10^{13.4}e^{-61\,600/RT}\qquad(1050°\text{–}1300°\mathrm{K}),$$

$$k_{\mathrm{C_4H_9SH}}=10^{13.3}e^{-55\,000/RT}\qquad(950°\text{–}1230°\mathrm{K}).$$

The results for the chloride and the bromide are in good agreement with those of other workers. The slight discrepancies that are present indicate that in the present work, in the temperature range 700°–950°K, the true reaction temperature behind the reflected shock is 10°–25°K lower than that computed in the usual manner.

INTRODUCTION

THE thermal decomposition reactions of *tert*-butyl chloride, bromide, alcohol, and mercaptan have been studied, using a single pulse shock tube. By this means, it is possible to extend the range of low-temperature results, thus imposing a critical test on the postulated mechanisms and rate constants. It is also expected that information could be obtained on the limitations of such shock-tube experiments.

There is general agreement that the tert-butyl compounds decompose unimolecularly through the formation of a four-center activated complex. The reaction is

$$t\text{-}\mathrm{C_4H_9X}=i\text{-}\mathrm{C_4H_8}+\mathrm{HX},$$

where X is the substituent group. Table I is a summary of the applicable earlier results.[1–7] It can be seen that, except for the alcohol, the discrepancies are not large. On the other hand, all of these reactions are extremely sensitive to wall effects, and in the previous studies disagreements have been explained by differences in the aging of the walls of the reaction vessel. In a shock tube, where the homogeneous heating and short reaction times completely remove the wall as a factor, heterogeneous effects are not present. Also, the short residence time ($\sim$1 msec) and the high dilution of the samples used ($\leq$1% in argon) would be expected to minimize chain reactions.

The main defect in the single-pulse shock-tube technique is in its use of the reflected shock as the heating element. As a result, there is an uncertainty with regard to the reaction temperature. Mark[8] has shown that the reflected shock temperature is lower than that computed under ideal one-dimensional conditions if the boundary layer behind the incident shock is laminar and the test gas has a low specific heat ratio γ (compared to that of a rare gas). For a turbulent boundary layer, Rudinger[9] has demonstrated that a temperature increase, resulting from the boundary layer–shock wave interaction, could be expected. Johnson and Britton[10] have recently compared the rate of $\mathrm{Br_2}$ decomposition in the incident and reflected shock regions. They concluded that in the reflected shock region the temperature is about 35°K below that calculated. The temperature range covered was 1500°–1900°K.

There have been numerous kinetic studies using the single pulse technique. In the temperature range that is of interest here (700°–1300°K), all the studies have concentrated on the decomposition of hydrocarbons.[11] This is somewhat unfortunate, since the complicated nature of these reactions and the uncertainty of the low-temperature results which are available make the assessment of these studies rather difficult. Recently, Lifshitz *et al.*[12] have studied the *cis–trans* isomerization reaction of 2-butene. The design of the single-pulse shock tube they used served as a pattern for the tube used in this investigation. The dump tank was placed at the low-pressure side of the shock tube close to the

---

[1] D. H. R. Barton and P. F. Onyon, Trans. Faraday Soc. **46**, 114 (1950).

[2] D. Brearly, G. B. Kistiakowsky, and C. H. Stauffer, J. Am. Chem. Soc. **58**, 43 (1936).

[3] S. C. Wong, Ph.D. Thesis, University of London (1958).

[4] G. B. Kistiakowsky and C. H. Stauffer, J. Am. Chem. Soc. **59**, 165 (1937).

[5] C. D. Harden and A. Maccoll, J. Chem. Soc. **1855**, 2454.

[6] B. F. Schultz and G. B. Kistiakowsky, J. Am. Chem. Soc. **56**, 395 (1934).

[7] J. A. Barnard, Trans. Faraday Soc. **55**, 947 (1959).

[8] H. Mark, NACA TM 1418.

[9] G. Rudinger, Phys. Fluids **4**, 1463 (1961).

[10] C. D. Johnson and D. Britton, J. Chem. Phys. **38**, 1455 (1963).

[11] G. B. Skinner and W. E. Ball, J. Phys. Chem. **64**, 1025 (1960). G. B. Skinner and E. M. Sokolski, J. Phys. Chem. **64**, 1028 (1960).

[12] A. Lifshitz, S. H. Bauer, and E. L. Resler, J. Chem. Phys. **38**, 2056 (1963).

diaphragm. Their results fall pretty well on the extrapolated low-temperature results, but there was a large amount of scatter. This might well have been caused by sampling problems.

TABLE I. Rate constants for the unimolecular elimination reaction of some *tert*-butyl compounds.

Compound	Rate constant (sec^{-1})	Temp. range (°K)	Ref.
t-butyl–Cl	$10^{12.4\pm0.2}\,e^{-41\,400\pm600/RT}$	563–614	1
	$10^{13.9\pm0.7}\,e^{-45\,000\pm1900/RT}$	547–624	2
	[a]$10^{13.77}\,e^{-45\,000/RT}$	563–603	3
t-butyl–Br	$10^{13.3}\,e^{-40\,500\pm1000/RT}$	509–565	4
	[a]$10^{14}\,e^{-42\,000/RT}$	503–553	5
t-butyl–OH	$10^{14.68}\,e^{-65\,500\pm7000/RT}$	760–823	6
	$10^{11.5\pm0.45}e^{-54\,500\pm1700/RT}$	760–893	7

[a] The uncertainties here should be the same as in Ref. 1.

EXPERIMENTAL

The single-pulse shock tube with the relevant dimension is shown in Fig. 1. It may be noted that the dump tank was placed at the low-pressure side of the shock tube instead of in its more conventional position at the end of the high-pressure section. The principal advantage of such an arrangement lies in the simplification of the necessary instrumentation and the much greater ease of operation. The gas dynamic effect of the dump tank was to damp out the numerous reflected shock waves that were bounced successively off the end walls. If unchecked, they would continually reheat the test sample. Together with the large volume of the dump tank, this damping action also helped to insure that the sample used for analysis suffered a minimum of contamination from mixing of sample and driver gas. The actual "starting up" process that occurs when the shock wave passes across the hole leading to the dump tank is extremely complex. Undoubtedly there is some weakening of the incident shock as it passes across the dump tank orifice. This is not of any importance since the sampling procedure used here precludes the use of this portion of the test gas for analysis. The subsequent behavior of the shock wave is more "normal" and is dealt with in the final section of this paper. A more complete discussion of the various aspects of this type of shock tube may be found in the work of Klepis[13] and Lifshitz *et al.*[12]

The shock velocities were measured by three $BaTiO_3$ pressure transducers placed near the end of the shock tube. The resulting signals were displayed on a raster on which was superimposed ten microsecond markers. It was possible to read the time to 1 μsec, but the actual uncertainties may be larger, due to the large size of the $BaTiO_3$ pressure elements ($\frac{1}{8}$ in.). A pressure history of the process was obtained from a Kistler quartz pressure pickup (Model 601) placed about 2 in. from the end plate. One or two layers of Cellophane were used as the diaphragm material and these were usually ruptured by a small solenoid-driven plunger. Helium was used as the driver gas for the low-temperature runs. For higher temperatures, hydrogen was used instead. The sampling port was placed at a point $\frac{1}{4}$ in. from the end wall. The distance between the gas sampling valve and the shock tube was kept small in order to minimize the dead space.

The procedure for a given run was the following:

(1) The dump tank was filled with argon to the pressure at which the experiment was to be carried out.

(2) The test section was evacuated to less than 1 μ. Under these conditions, the leak rate was usually 1–2 μ/min.

(3) After filling the low-pressure section with the test gas, the ball valve joining it with the dump tank was opened.

(4) The high-pressure section was filled, the diaphragm was ruptured, and a sample of about 10 cc (NTP) was taken for analysis.

In order to minimize the effect of diffusion, the last two steps were carried out as rapidly as possible (several seconds). The 10 cc used for analysis represented from 2% to 8% of the total test gas.

The gas analysis was carried out with a Beckmann GC-2 chromatograph using a 6- or 10-ft ethyl hexylsebacate column (30% on firebrick) at 40°C. Helium was the carrier gas. Under the conditions of these experiments, the minimum measurable percentage conversion was 0.1%. Isobutene and the parent compound were both eluted from these columns and it was thus possible to make a mass balance. In all cases, the balance was satisfactory. This indicated that no driver gas was mixed with the sample of test gas taken for analysis.

Various concentrations of the butyl compound were used in these studies. In no case was the mole fraction greater than 0.01. Matheson Pure Grade argon listed at 99.998% was the diluent. No attempt was made at further purification. The *tert*-butyl halides and alcohol were Eastman Grade chemicals, while the mercaptan was an API sample. These were also used without further purification. They were degassed and only the middle fractions of a given sample were used. Initial pressures of the test gas ranged from 80 to 350 mm Hg.

COMPUTATIONS

The reflected shock temperatures were computed on the basis of ideal one-dimensional theory, using the measured incident shock velocity. The necessary thermodynamic data for the halides and the alcohol were calculated from the vibrational assignments of Shep-

---

[13] J. E. Klepis, M.Sc. Thesis, Cornell University (1961).

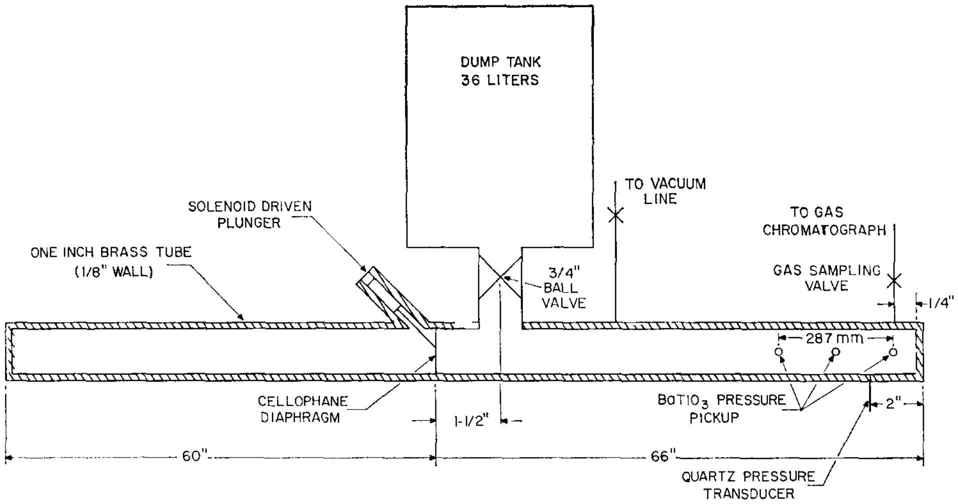


FIG. 1. Single-pulse shock tube used in the present studies.

pard[14] and Pritchard and Nelson.[15] The barrier to internal rotation was that determined by Howlett.[16] The thermodynamic data for the mercaptan were taken from the work of McCullough *et al.*[17] Due to the high dilution and low enthalpy of reaction, it was not necessary to correct for the heat input due to chemical reaction (in the 1% mixture where this would begin to be significant, the amount of conversion was kept below 25%). As mentioned earlier, the temperature so computed was uncertain due to the nonidealities that were present. In the present case, the temperature lowering effect should not be too significant, since, with the high

TABLE II. Summary of data for the unimolecular elimination of HCl from *t*-butyl chloride.

Composition of test mixtures	T (°K) (reaction temp.)	t (msec) (dwell time)	Final density (mm Hg) $p_1(\rho_5/\rho_1)$	% conversion	Rate constant k (sec^{-1})
1% t-C_4H_9Cl in argon	771	1.60	676	0.9	5.8
	757	1.60	1310	0.55	3.4
	766	1.55	1307	0.8	5.4
	805	1.50	706	3.4	23.2
	814	1.45	710	3.8	26.4
	805	1.45	605	3.1	21.4
	860	1.30	572	19.0	162.5
	805	1.50	444	3.1	21.4
	848	1.40	631	10.3	77.5
½% t-C_4H_9Cl in argon	817	1.60	557	7.4	47.5
	810	1.55	629	3.2	20.3
	810	1.50	629	3.4	22.7
	856	1.40	581	18.1	142.0
	864	1.35	585	20.95	174.0
	775	1.60	640	1.3	8.1
	781	1.55	646	1.4	9.1
	846	1.45	614	11.3	82.2
	840	1.45	616	12.3	90.2
⅛% t-C_4H_9Cl in argon	955	1.30	1000	86.3	1510.0
	925	1.40	1018	73.8	956.0
	955	1.20	960	88.2	1800.0
	912	1.30	549	57.5	660.0
	920	1.30	551	66.0	831.0
	826	1.50	565	6.6	45.6
	927	1.30	326	72.2	990.0
0.226% t-C_4H_9Cl and 1% C_3H_6 in argon	872	1.35	576	23.9	202.0
	895	1.25	564	40.5	417
	941	1.20	561	70.7	1020.0
	825	1.45	619	5.0	34.8
	825	1.45	580	5.0	34.0
	899	1.25	565	38.5	393.0

---

[14] N. Sheppard, Trans. Faraday Soc. **46**, 527 (1950).

[15] J. G. Pritchard and H. M. Nelson, J. Phys. Chem. **64**, 795 (1960).

[16] K. E. Howlett, J. Chem. Soc. **1951**, 1409; **1955**, 1784; **1957**, 2831.

[17] J. P. McCullough, D. W. Scott, H. L. Finte, W. N. Hubbard, M. E. Gross, C. Katz, R. E. Pennington, J. F. Messerly, and G. Waddington, J. Am. Chem. Soc. **75**, 1818 (1953).

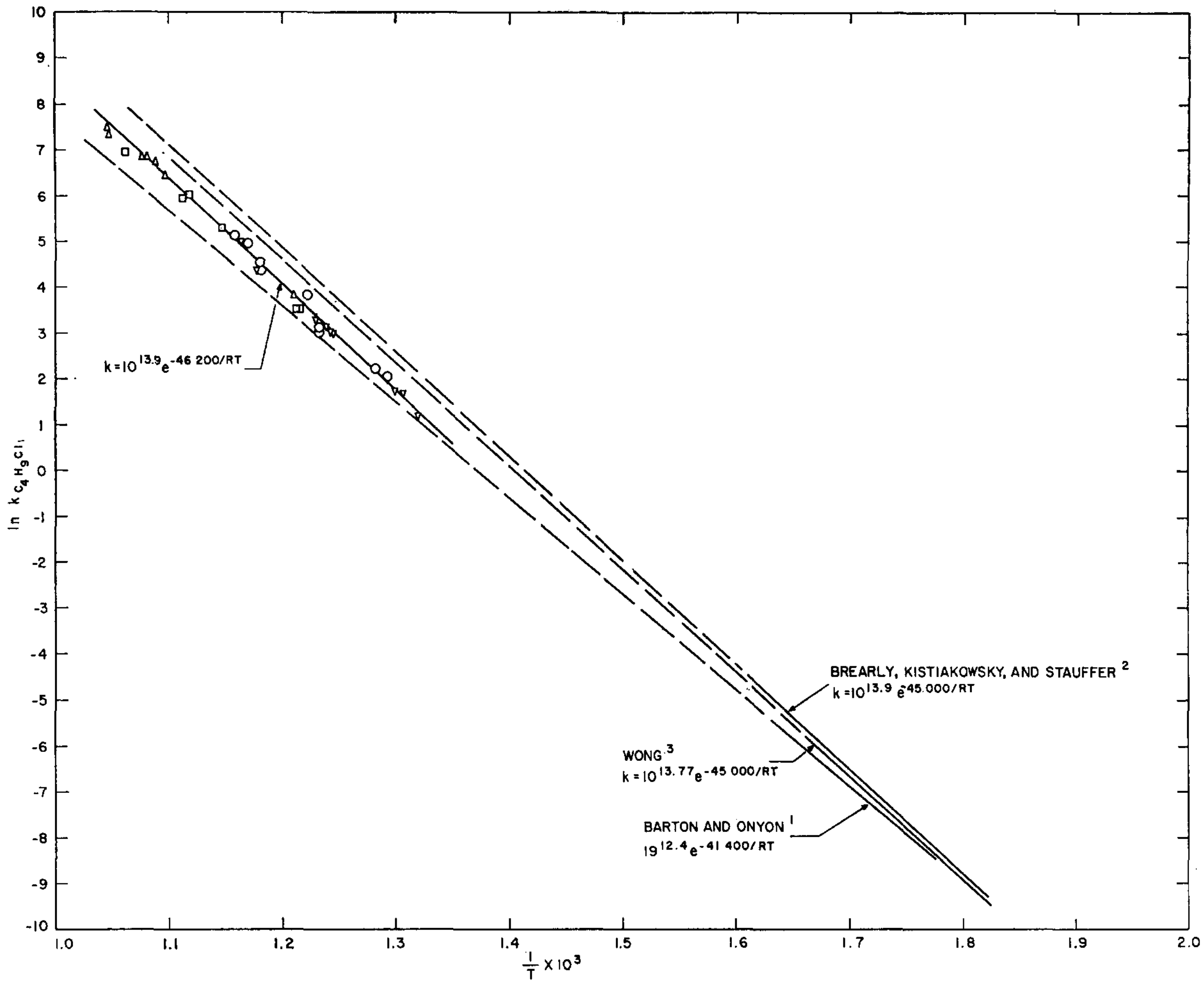


FIG. 2. Rate constants as a function of $1000/T$ (°K^{-1}) for the decomposition of *t*-butyl chloride ($t\text{-}C_4H_9Cl \longrightarrow i\text{-}C_4H_8 + HCl$) $\nabla = 1\%$ C_4H_9Cl in argon; $\bigcirc = \frac{1}{2}\%$ C_4H_9Cl in argon; $\Delta = \frac{1}{8}\%$ C_4H_9Cl in argon; $\square = 0.226\%$ C_4H_9Cl, 1% C_3H_6 in argon.

dilutions used, the test gas closely approximated a rare gas ($\gamma = 1.61$ for the worse case). The interaction due to the turbulent boundary layer as described by Rudinger[10] may be quite important; this would cause a temperature increase. An additional complication introduced here was the unconventional position of the dump tank; this may result in a lowering of the temperature. Some experimental observations will be recorded later. For the present work, these effects would be reflected chiefly in the pre-exponential term of the rate expression, since the magnitude of the temperature deviations did not vary greatly in going through the 200°–250°K range used here.

The dwell time was taken to be the time between the arrival of the reflected shock and the onset of the expansion wave as measured by the quartz pressure pickup. This was another source of uncertainty, since the degree of mixing within the shock tube would have a major bearing on what the true dwell time should be. Unfortunately, it was not possible to make an exact determination of the diffusion between the different layers of the reacted gas, each of which had its own history. In these experiments, mixing appeared to have been minimized due to the following observations. First, as was mentioned previously, there was never any driver gas in the sample used for analysis. Second, in runs with different densities but at the same temperature, there were no systematic differences in percentage conversion. Aside from proving the unimolecularity of these reactions, one would expect that if mixing were important, the lower density runs would also show lower percentage reaction. Finally, there was no problem in obtaining virtually 100% reaction (for the *t*-butyl bromide, there was a back reaction which seemed to be catalyzed by the sampling system: as a result complete reaction was obtained only for the $\frac{1}{6}\%$ runs). The values of the dwell time used here assumed that the sample taken for analysis was representative of the constitution of that 25% of the test gas that was nearest the end wall. The "true" dwell time may range from 20% longer (no mixing) to 60% shorter (complete mixing). This uncertainty should not have any large effect on the activation energy since it would be carried over for each run.

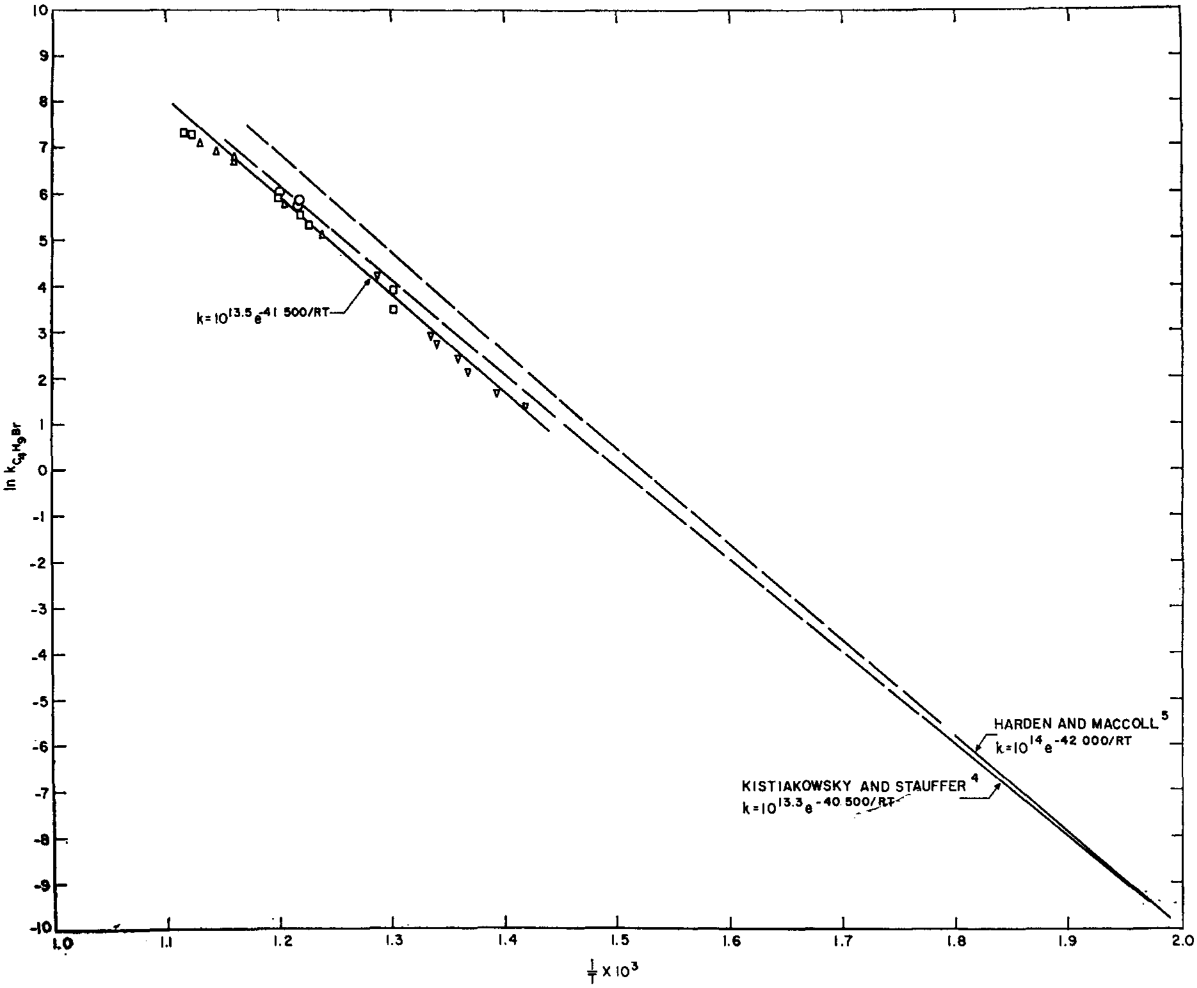


FIG. 3. Rate constants as a function of $1000/T$ (°K^{-1}) for the decomposition of *t*-butyl bromide ($t\text{-}C_4H_9Br \xrightarrow{k_{C_4H_9Br}} i\text{-}C_4H_8+HBr$). $\nabla=1\%$ C_4H_9Br in argon; $\bigcirc=\frac{1}{3}\%$ C_4H_9Br in argon; $\Delta=\frac{1}{6}\%$ C_4H_9Br in argon; $\square=0.146\%$ C_4H_9Br, 0.61% C_3H_6 in argon.

RESULTS

a. *t*-Butyl Chloride and *t*-Butyl Bromide

The stoichiometry of the thermal decomposition was simply

$$t\text{-}C_4H_9Cl \xrightarrow{k_{C_4H_9Cl}} i\text{-}C_4H_8+HCl$$

$$t\text{-}C_4H_9Br \xrightarrow{k_{C_4H_9Br}} i\text{-}C_4H_8+HBr,$$

where the rate constant k was obtained from the expression

$k=1/t \ln c_0/c_f$,

$t=$ dwell time,

$c_0=$ initial concentration of *t*-butyl compound,

$c_f=$ final concentration of *t*-butyl compound.

There was no need to consider the back reactions, since, under the conditions of these experiments, the equilibrium constants favored decomposition overwhelmingly. Addition of large amounts of propylene, changing the total pressure by a factor of ∼3 and changing the percentage of reactant molecules (by a factor of 6 for the bromide and a factor of 8 for the chloride) did not cause any systematic change in the rates of the reaction. There were no side products. These results confirmed the previous conclusion that the decomposition reaction is unimolecular and that k is the limiting high-pressure rate constant. This is not surprising considering the complexity of the molecules and the relatively high reaction pressures used. It is also clear that the reaction does not involve free radicals. Table II summarizes the data for the chloride system and is representative of the results obtained for the other *t*-butyl compounds. The usual Arrhenius plots are shown in Figs. 2 and 3. The temperature range covered was 700°–900°K for the bromide and 750°–950°K for the chloride. Also plotted on the same figures are all the low-temperature results. From the shock-tube results obtained in this study, the

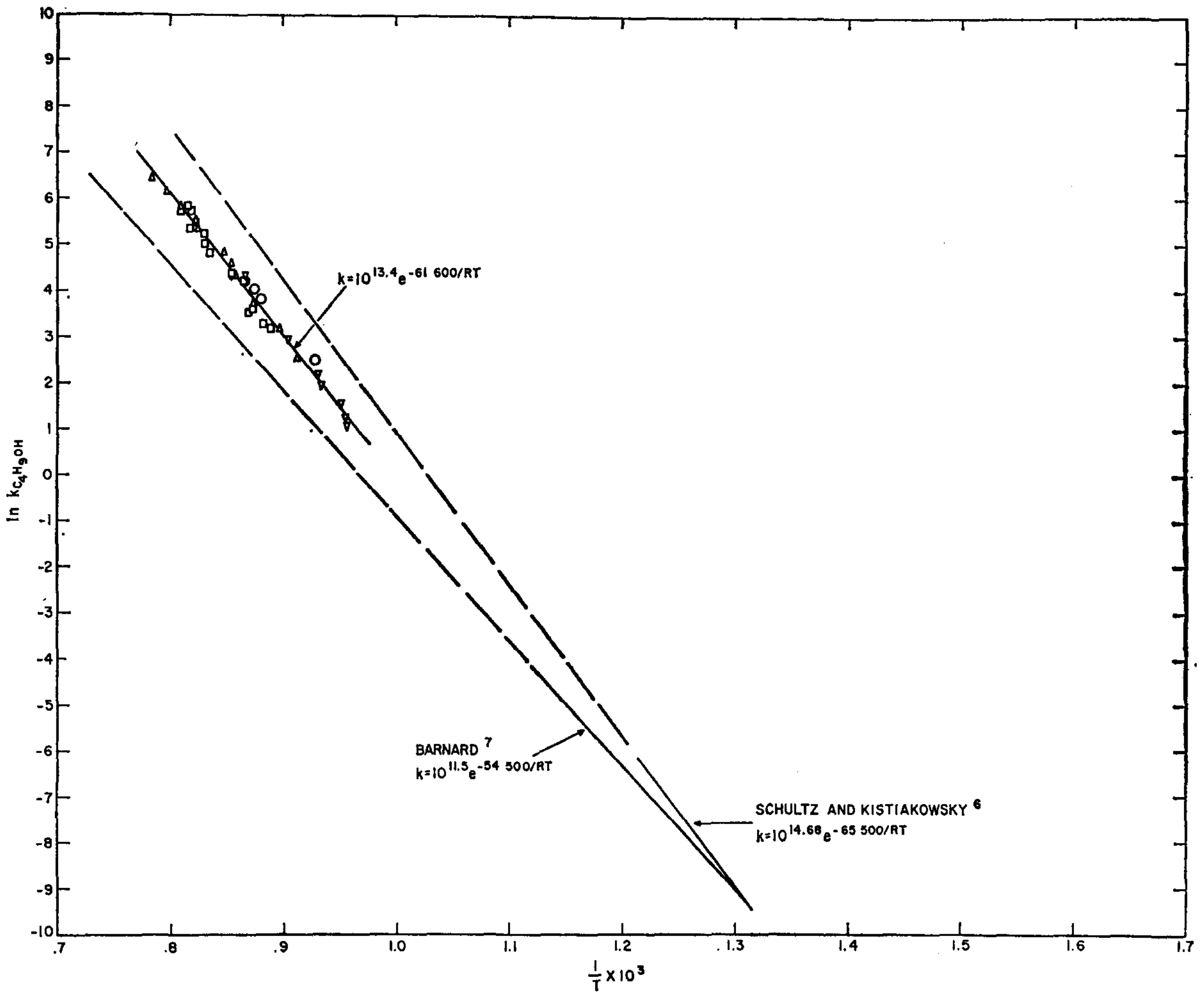


FIG. 4. Rate constants as a function of $1000/T$ (°K^{-1}) for the decomposition of *t*-butyl alcohol ($t\text{-}C_4H_9OH \xrightarrow{k_{C_4H_9OH}} i\text{-}C_4H_8+H_2O$). ▽ = 1% C_4H_9OH in argon; ○ = ½% C_4H_9OH in argon; △ = ¼% C_4H_9OH in argon; □ = ¼% C_4H_9OH, 1% C_3H_6 in argon.

rate expressions were found to be

$$k_{t\text{-}C_4H_9Cl}=10^{13.9}e^{-46\,200/RT},$$

$$k_{t\text{-}C_4H_9Br}=10^{13.5}e^{-41\,500/RT}.$$

It was difficult to give an exact estimate of the limits of confidence since the key uncertainties arose from systematic errors whose magnitudes were not well defined. As a rough estimate, the rate constants obtained here were probably accurate to within a factor of 2 or 3. The systematic nature of these errors would tend to minimize the resulting uncertainty in the activation energy. As a result in activation energy, the error here (for the chloride and bromide case) was probably less than 7%. If the best straight line is drawn between the high- and low-temperature results, one obtains a slightly lower activation energy (~1.5 kcal less). The systematic errors that are present in this study, however, makes such a procedure very doubtful.

b. *t*-Butyl Alcohol

In general, the decomposition of the alcohol was similar to that of the halides. The addition of propylene, increasing the pressure and changing the concentration of reactants, did not cause any systematic change in the percentage conversion. The main reaction appears to be the unimolecular elimination

$$t\text{-}C_4H_9OH \xrightarrow{k_{C_4H_9OH}} i\text{-}C_4H_8+H_2O.$$

The alcohol is more stable than the halides and thus a higher temperature range (1050°–1300°K) was needed. An additional complication was brought about by the presence of side products. For example, at about 60% reaction in a 1% mixture, the product distribution was approximately 50% isobutene, 7% allene, and smaller amounts of propylene, isobutane, and acetone. These might have been formed as a result of decomposition

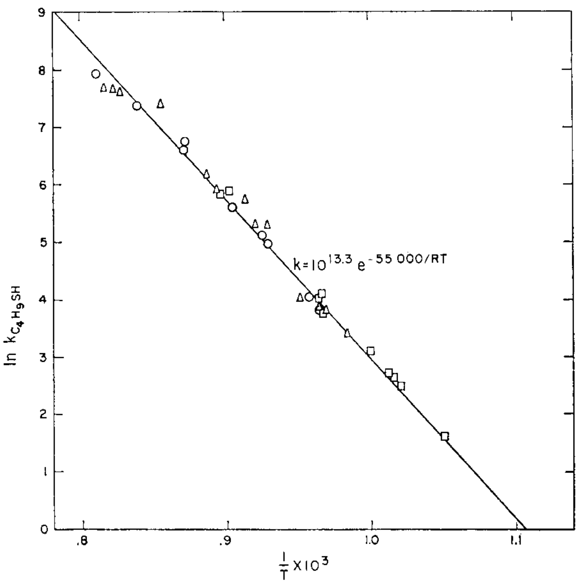


FIG. 5. Rate constants as a function of $1000/T$ (°K^{-1}) for the decomposition of t-butyl mercaptan

$(t\text{-}C_4H_9SH\xrightarrow{k_{C_4H_9SH}}i\text{-}C_4H_8+H_2S)$.

○ = 0.1% C_4H_9SH, 1.0% C_3H_6 in argon;

Δ = 0.1% C_4H_9SH, 0.3% C_3H_6 in argon;

□ = 0.375% C_4H_9SH, 1.125% C_3H_6 in argon.

of isobutene. The mechanism probably involves

$$C_4H_8\rightarrow C_4H_7+H$$

$$H+C_4H_8\rightarrow C_4H_7+H_2$$

$$H+C_4H_9OH\rightarrow C_4H_8OH+H_2$$

$$C_4H_7\rightarrow C_3H_4+CH_3$$

$$C_4H_8OH\rightarrow CH_3COCH_3+CH_3\quad\text{etc.}$$

When the temperature was lowered, the relative amount of side products (compared to the isobutene produced) was decreased. Accordingly, the highest temperature used was 1300°K. At this point, about 20% of the alcohol was converted to isobutene and the side products were less than 1% of the former. The results were plotted in the usual manner in Fig. 4. As before, the low-temperature data were also included. The rate of expression was the following:

$$k_{C_4H_9OH}=10^{13.4}e^{-61\,600/RT}.$$

The uncertainty here was of the same magnitude as that of the chloride and bromide (7% in activation energy).

c. *t*-Butyl Mercaptan

The decomposition of the mercaptan was different from those of the other tertiary butyl compounds, in that concurrent with the unimolecular elimination, there appeared to be a radical process. As a result, at about 1000°K, the extent of reaction for a 1% mixture was a factor of 2.5 greater than that of a $\frac{1}{4}$% mixture and a factor of 4 greater than those of mixtures with varying amounts of propylene. For the study of the inhibited reaction, the propylene–mercaptan ratios used were three to one and ten to one, the concentration of the mercaptan was 0.1 and 0.375 percent and the densities ranged from 400 to 1000 mm Hg (NTP). The results, as summarized in Fig. 5, showed no systematic deviations and it was concluded that the radical process had been completely suppressed. The residual reaction was that of unimolecular elimination:

$$t\text{-}C_4H_9SH\rightarrow i\text{-}C_4H_8+H_2S.$$

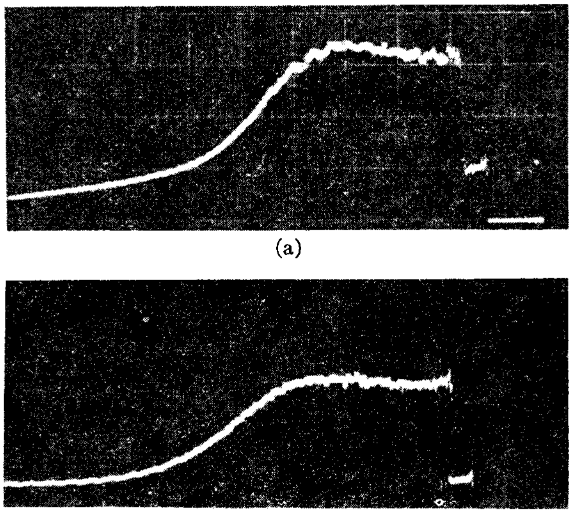
The rate expression was:

$$k=10^{13.3}e^{-55\,000/RT}.$$

The error was the same as given above.

DISCUSSION

In the temperature range 700°–900°K, the results, as summarized in Figs. 2 and 3, are in good agreement with most of the previous work. It will be noted that, except for the work of Barton and Onyon,[1] the activation energies obtained parallel closely the earlier values, while the absolute values of the rate constants appear to be smaller than the extrapolated low-temperature results. Assuming the correctness of the earlier works, this would mean that the temperatures attained in these experiments are slightly lower by about 10°–25°K than those calculated. This temperature defect is probably due to the nonidealities mentioned previously, but small systematic errors in velocity measurement and dwell time determination may also play a part. As was



(a)

(b)

FIG. 6. (a) Typical pressure record of shock in dilute mixtures of t-butyl chloride in argon. Time scale—500 μsec/cm. Pressure scale—arbitrary. $M\sim1.8$. Dump tank was not used. (b) Approximately the same as above, but with dump tank.

mentioned earlier, the work of Barton and Onyon[1] was discordant. This is most unfortunate since their study appeared to be the most careful of the whole set. If their values were the correct ones, it would mean that the temperature was slightly higher than that computed. This would not be very discomfiting in itself. However, the large discrepancy in activation energy, 41.4 to 46.2 kcal, is a more serious matter and is rather difficult to explain in light of the previous analysis. Acceptance of the lower value would also require that for the bromide system, which was studied under the same conditions as the chloride, the activation energy be lowered to 37 kcal. This is lower than any previous determination.

In making these comparisons, it is assumed that the Arrhenius equation is strictly valid. This should be a good approximation, for although the total temperature range covered is larger than usual (500°–950°K), any curvature in the Arrhenius plot would become important only if the pre-exponential factor is very strongly temperature dependent. There also should not be any deviations due to energy exchange effects, since each molecule suffers about 10^7 collisions with the argon diluent during the ~ 1 msec of reaction. The independence of the extent of reaction with pressure is, of course, a good confirmation of this.

The rate constants for the decomposition of the alcohol obtained in this work fall between those of Schultz and Kistiakowsky[6] and that of Barnard.[7] The large uncertainty ($E = 65.5 \pm 7$ kcal) in the former work prevents any meaningful comparison. The discordance of the present result with the work of Barnard[7] seems to be too large to be explained in terms of an error in the temperature determination. It is possible that, in the present case, there is a contribution by radical reactions of various types. On the other hand, one would expect that changing the reactant composition and adding propylene would have caused some striking effects if this were true. The pre-exponential factor ($10^{11.54}$) obtained in the earlier study seems to be low and is in fact quite different from that of any other four-center elimination reaction involving a hydrogen atom.

The only previous study on the kinetics of the decomposition of *t*-butyl mercaptan appears to be that of Thompson, Meyer, and Ball,[18] using a flow system. They found that the pyrolysis proceeded by a free radical mechanism which was inhibited by toluene. No attempt was made to study the fully inhibited reaction. In the present work, the appearance of the radical reaction is understandable when one notes that the difference between the C–SH bond energy (69.14 kcal/mole[19]) and the activation energy for elimination (55 kcal) is only 14.4 kcal. For the *tert*-butyl chloride, bromide, and alcohol, the difference comes out to be 32, 21, and 27 kcal, respectively. The rate expression for the fully inhibited reaction is about what one would expect for a unimolecular elimination of this type. A linear relationship between the ion dissociation energy $D(\mathrm{R}^+ - \mathrm{X}^-)$ and the activation energy for the elimination of the hydrogen halides from various alkyl halides has been noted by Maccoll.[20] Application of such an empirical relationship to the mercaptan system yields an activation energy of 52 or 57 kcal, depending on the ΔH_f chosen for the SH^- ion.[21] As a matter of fact, such a relation would predict an activation energy of 59.2 kcal for the alcohol. The value obtained here was 61.6 kcal.

From the above discussion, it appears that the true temperature is, if anything, slightly lower than the value that is computed. This is contrary to the work of Rudinger[10] and must be due to the attenuating effect of the dump tank. That the dump tank must inevitably have an attenuating effect is clear, since the sound speed behind the incident shock is greater than the shock speed. In the present study, there does not appear to be an attenuation in the incident shock velocity. This may be due to the experimental setup. All that can be said with certainty is that in the last 6 in. of the shock tube the deceleration in velocity is less than $\frac{1}{2}\%$. The pressure-time traces, however, show the effect of the dump tank very well. Figure 5(a) shows a trace taken without the dump tank. The initial dip may be due to the mounting since it is present in the incident shock also, but it is clear that there is a gradual pressure increase. This is similar to the observation by Rudinger[10] Using the isentropic relationship, which is a good approximation in the present case, the pressure rise is found to be equivalent to a temperature increase of approximately 40°K. With the dump tank operating, the pressure trace, as seen in Fig. 6(b), seems to have been flattened out. It would thus appear that the rarefaction waves from the dump tank have cancelled the pressure waves from the shock wave turbulent boundary layer interaction. The above pictures suggest that the attenuation due to the dump tank, if properly used, may be quite helpful in securing a more constant reaction temperature for the test gas near the end of the shock tube. This could make all the more important proper sampling and extremely accurate measurements of the shock velocity and pressure.

ACKNOWLEDGMENTS

The author wishes to thank Dr. R. E. Ferguson for his constant encouragement and his constructive suggestions in the preparation of the manuscript. He is also indebted to his wife, Dr. S. C. Wong, for many helpful discussions.

---

[18] C. J. Thompson, R. A. Meyer, and J. S. Ball, J. Am. Chem. Soc. **74**, 3287 (1953).

[19] T. Cottrell, *Strength of Chemical Bonds* (Butterworths Scientific Publications Ltd., London, 1958).

[20] A. Maccoll, *Carbonium Ions, Real and Virtual, and Their Rearrangement in the "Transition State"*, edited by G. Porter (The Chemical Society, London, 1962).

[21] F. Field and J. Franklin, *Electron Impact Phenomena* (Academic Press Inc., New York, 1957).