

addition,  $\lambda_1$ , obtained from excimer decay curves, is shown in Figure 7 at several *n*-hexane pressures. For these data, open circles are used, and the right-hand axis pertains. The exciting wavelength used in these experiments was 2559 Å (the 0-0 band of  $S_1 \leftarrow S_0$ ), and therefore vibrational relaxation effects (in the monomer manifold) would be very slight or absent.

From the data shown in Figure 7, the pressure coefficient of  $\lambda_2$  (between 0 and 30 Torr) is about  $6 \times 10^9 M^{-1} \text{sec}^{-1}$ . Since the decrease in the monomer quantum yield indicated in Figure 6 for  $\lambda_{\text{exc}}$  of 249 nm is considerably less than the increase in  $\lambda_2$  throughout the corresponding *n*-hexane pressure range, it can be concluded that both  $k_{fM}$  and  $k_{iM}$  are pressure dependent. The determination of the pressure coefficients of  $k_{fM}$  and  $k_{iM}$ , individually, is made rather difficult by the complexity of  $\lambda_2$  (see eq 3), but, presumably, the pressure coefficient of  $k_{fM}$  is greater than that for  $k_{iM}$ . It is also possible that part of the increase in  $\lambda_2$  (and the enhancement in the excimer emission intensity) can be attributed to increased excimer formation efficiency at higher *n*-hexane pressures (*i.e.*, a pressure-dependent  $k_{DM}$ ). Thus, termolecular processes may be important in the ABCO excimer formation.

Observations of pressure dependent radiative and nonradiative rate constants in saturated amine systems

have been made before. In these cases, the pressure coefficient of  $1/\tau_f$  was also about  $10^9 M^{-1} \text{sec}^{-1}$ . The apparently large (*n*-hexane) pressure dependence of  $k_{fM}$  may be a consequence of the Rydberg nature of the excited state(s) of saturated amines.<sup>17,18</sup> External pressure effects on the absorption spectra of Rydberg transitions have been examined by Robin and Kuebler<sup>19</sup> but at much higher pressures.

It is evident from Figure 7 that there is only a very slight effect on  $\lambda_1$  by increasing the *n*-hexane pressure. This is a consequence of the diminished susceptibility of the excimer to collisional perturbation and implies that the excimer state is shielded because of the "head-to-head" configuration.

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## Gas Phase Thermal Decomposition of *tert*-Butyl Alcohol

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**Abstract:** The homogeneous, gas phase, thermal decomposition of *tert*-butyl alcohol to isobutene and water was studied in a single-pulse shock tube. The comparative rate technique was used, with the decyclization of cyclohexene to ethylene and 1,3-butadiene serving as the internal standard reaction. Over the temperature range 920–1175°K, the comparative rate data for unimolecular *tert*-butyl alcohol decomposition were fit well by the expression  $\log k (\text{sec}^{-1}) = 14.6 - (66.2 \times 10^3/4.58T^\circ\text{K})$ .

The gas phase thermal decomposition of *tert*-butyl alcohol has been the subject of a number of previous studies<sup>1-4</sup> (see Table I). Schultz and Kistiakowsky (S and K),<sup>1</sup> using a static reactor, determined that the primary reaction was the molecular elimination to form isobutene and water and that the reaction was first order down to 3 Torr, below which pressure falloff was encountered. Barnard,<sup>2</sup> working in a similar temperature and pressure range, obtained rate constants that agree with those reported by S and K at 760°K but which were considerably lower than those reported by S and K at higher temperatures. Thus his deduced activation energy value was lower (54.5 *vs.* 65.5 kcal). Tsang<sup>3</sup> studied the reaction at higher temperatures in a single-pulse shock tube and measured rate constants that fell between values predicted from extrapolation of

Table I. Results of Earlier Studies of *tert*-Butyl Alcohol Pyrolysis

<i>T</i> range, °K	<i>P</i> range, Torr	$\log k, \text{sec}^{-1}$	Ref
760-828	1-344 <sup>a</sup>	$14.68 - [(65,500 \pm 7,000)/4.58T^\circ\text{K}]$	1
760-893	20-400	$(11.51 \pm 0.45) - [(54,500 \pm 1,700)/4.58T^\circ\text{K}]$	2
1050-1300	<i>b</i>	$13.4 - [(61,500 \pm 4,300)/4.58T^\circ\text{K}]$	3
	<i>b</i>	$(13.35 \pm 0.20) - [(60,500 \pm 100)/4.58T^\circ\text{K}]$	4

<sup>a</sup> Onset of falloff noted at about 3 Torr, at 789°K. <sup>b</sup> These data are not reported.

S and K's and Barnard's Arrhenius plots. Dorko, *et al.*, have reported shock tube results essentially identical with Tsang's. Their study was run as a means of verifying proper operation of their shock tube in preparation for the study of other reactions. Workers in other laboratories<sup>5,6</sup> have also used this reaction for that purpose.

(5) H. F. Carroll, Ph.D. Thesis, Cornell University, 1969.

(6) D. K. Lewis, Ph.D. Thesis, Cornell University, 1970.

(1) B. F. Schultz and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **56**, 395 (1934).

(2) J. A. Barnard, *Trans. Faraday Soc.*, **55**, 947 (1959).

(3) W. Tsang, *J. Chem. Phys.*, **40**, 1498 (1964).

(4) E. A. Dorko, D. B. McGhee, C. E. Painter, A. J. Caponecchi, and R. W. Crossley, *J. Phys. Chem.*, **75**, 2526 (1971).

Recently, the *tert*-butyl alcohol decomposition has been used as a standard reaction in the single-pulse shock tube relative rate technique developed by Tsang.<sup>7</sup> In this technique, two noninteracting unimolecular reactions are studied simultaneously, and the extent of reaction of one is used to determine the reaction temperature. This procedure has allowed a great reduction in the scatter of shock tube data as compared with the absolute temperature measurement method, based on incident or reflected shock velocities. Jeffers and Shaub,<sup>8</sup> and Jeffers<sup>9</sup> have reported rate constants for a number of *cis*-*trans* isomerization reactions relative to *tert*-butyl alcohol decomposition. Also, Jeffers<sup>10</sup> Lewis and Sarr<sup>10</sup> have performed independent studies of cyclopropane isomerization and Lewis, *et al.*,<sup>11</sup> have studied cyclopentene dehydrogenation relative to *tert*-butyl alcohol. Despite the high precision of the relative rate technique, the accuracy of rate parameters deduced for a reaction under study cannot be any better than those of the reaction used as the standard. In studying the cyclopropane isomerization<sup>10</sup> and cyclopentene decomposition,<sup>11</sup> we uncovered inconsistencies which prompted us to question the accuracy of the Arrhenius parameters reported by Tsang<sup>3</sup> and which led us to conduct the study reported here.

In this paper we report a single-pulse shock tube study of the decomposition of *tert*-butyl alcohol to isobutene and water, using the relative rate technique. The unimolecular decyclization of cyclohexene to form ethylene and 1,3-butadiene served as the internal standard reaction. Tsang<sup>12,13</sup> has reported two careful studies of cyclohexene, and his results are in excellent agreement with the lower temperature work of Uchiyama, Tomioka, and Amano.<sup>14</sup> This reaction appeared to be an excellent reference for *tert*-butyl alcohol and hence for the other reactions referred to above.

## Experimental Section

**Apparatus and Method.** We used a 10-cm i.d., stainless steel, single-pulse shock tube of the "magic hole" design,<sup>15</sup> which is believed to be the largest shock tube of this type reported in the literature. The experimental section has a length of 3.66 m and the high-pressure section is adjustable, with a maximum length of 1.83 m. Aluminum diaphragms were used. The tube was routinely evacuated to a pressure below  $10^{-3}$  Torr before the experimental mixture was introduced, and leak/outgassing rates did not exceed  $2 \times 10^{-4}$  Torr/min. Samples were usually in the shock tube for 30 sec to 1 min before being shocked. Incident shock speeds were measured by displaying the signals from two BaTiO<sub>3</sub> pressure transducers, located 24.834 and 14.836 cm for the downstream end of the tube, on an oscilloscope trace calibrated with 1  $\mu$ sec time markers. Shock arrival times could be measured to  $\pm 0.25$   $\mu$ sec. High-temperature reaction times were measured with a third pressure detector (Kistler) located 4.834 cm from the end of the tube. Reactant and product samples amounting to about 20 cm<sup>3</sup> of gas were taken from a port 9.835 cm from the end of the tube. Because of the small sample size and the relative positioning of the

sampling port and pressure gauge used for measuring dwell times, it was concluded that no "time averaging" corrections to the measured dwell times were necessary.<sup>15</sup> Occasionally the third pressure detector was also used as a velocity gauge so that two incident shock velocity measurements could be obtained from an experiment. The twin velocity measurements never varied by more than  $\pm 0.5$   $\mu$ sec and showed no systematic variation; so shock attenuation or speed-up after the first two gauges was not considered to be a problem. The uncertainty in incident shock velocity measurements accounts for an uncertainty of  $\pm 15^\circ$  K in reflected shock temperatures.

The shock tube was "tuned" by varying length of the driver section so that the reflected shock wave, contact surface between sample and driver gas, and expansion wave reflected from the end of the driver section all met simultaneously and generated the most rapid expansion wave to cool the heated gas. The optimum condition was determined empirically from oscilloscope displays of the output of the third pressure detector. Reaction times before the onset of cooling ranged from 800 to 900  $\mu$ sec. Because of difficulties in simultaneously maintaining constant reaction pressure and temperature, experienced by other workers using the "tailored interface" technique to increase reaction times,<sup>16</sup> that mode of operation was not used.

To ensure that proper single-pulse operation, with no mixing of driver and sample gases, had been achieved, pure argon was shocked to 1200–1500°K with a driver gas consisting of helium to which a substantial amount of *n*-butane had been added. Samples removed from the tube immediately after shocking showed no trace of any hydrocarbon upon gas chromatographic analysis, verifying that no mixing had occurred. Samples removed 15–30 min after heating, after diffusive mixing had occurred, showed substantial quantities (up to 1%) of *n*-butane but no other hydrocarbon.

Because the cooling process is not abrupt, there is some product formation after the onset of cooling. Our shock tube, properly turned, has an initial cooling rate of  $\sim 2 \times 10^5$  °K/sec, from a shocked gas temperature of 1200°K. By integrating over the 800- $\mu$ sec reaction time plus the cooling process, we estimate that, for a first-order reaction with an activation energy of 65 kcal/mol, approximately 20% of the product can be attributed to reactions occurring during the cooling process. This percentage increases with reaction temperature if the initial cooling rate is constant. However, the cooling rate also increases with reflected shock temperature and compensates for this. As a result, the percentage of products produced during the cooling process should be relatively constant over the temperature range covered by these experiments. Therefore, activation energy values deduced from Arrhenius plots, using temperatures calculated from measured shock speeds, should not be significantly affected, although deduced preexponential factors may be slightly higher than actual values. In this study, all reaction was assumed to have occurred during the 800–900- $\mu$ sec reaction time; no adjustments were made for the finite cooling process. It should be noted that the finite quench period will have no effect on Arrhenius parameters determined *via* the relative rate method, so long as the reaction under investigation and the standard reaction have the same reaction order and similar activation energies.

**Materials and Sample Preparation.** The *tert*-butyl alcohol was Brothers Chemical Co. "Reagent Grade," and the cyclohexene used as the relative rate standard was Matheson Coleman and Bell "Research Grade." The sample reagents were purified by triple distillation under vacuum in a glass system which could be pumped down to below  $1 \times 10^{-5}$  Torr. Gas chromatographic analysis showed no detectable impurities. The purified reagents were then transferred to stainless steel tanks which were immediately pressurized to about 75 psia with Matheson "Ultra High Purity" argon. The gases were allowed to mix for at least 3 days, and usually more than a week, before use. Tank pressure was checked before use to see that no leakage had occurred. To prevent possible contamination by inward leakage of air, a new sample mixture was prepared whenever the pressure in a tank reached 1 atm, through use.

Matheson "C.P. Grade" methane, ethane, ethene, propene, allene, isobutene, and 1,3-butadiene were used as obtained from the lecture bottles for preparation of gas chromatograph calibration mixtures.

**Analyses.** Reactant and product samples were withdrawn from

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(8) P. M. Jeffers and W. Shaub, *J. Amer. Chem. Soc.*, **91**, 7706 (1969).

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(12) W. Tsang, *J. Chem. Phys.*, **42**, 1805 (1965).

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(14) M. Uchiyama, T. Tomioka, and A. Amano, *J. Phys. Chem.*, **68**, 1878 (1964).

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

(16) (a) T. A. Brabbs and F. E. Belles, 5th International Shock Tube Symposium Proceedings, U. S. Naval Ordnance Laboratory, Silver Spring, Maryland, 1966, pp 955–968; (b) F. E. Belles, private communications.

Table II. Experimental Conditions

Set	Symbol	% <i>tert</i> -butyl alcohol	% cyclohexene	Initial sample pressure range, Torr	Conditions behind reflected shocks		
					Pressure range, Torr	Relative rate	T range, °K Shock velocities
A	○	0.215	0.215	35-65	710-940	960-1162	947-1142
B	●	1.00	0.50	28-56	670-910	923-1176	904-1182
C	▽	0.25		65-120	1340-1560		937-1210
D	▼	1.03		16-28	370-410		935-1175

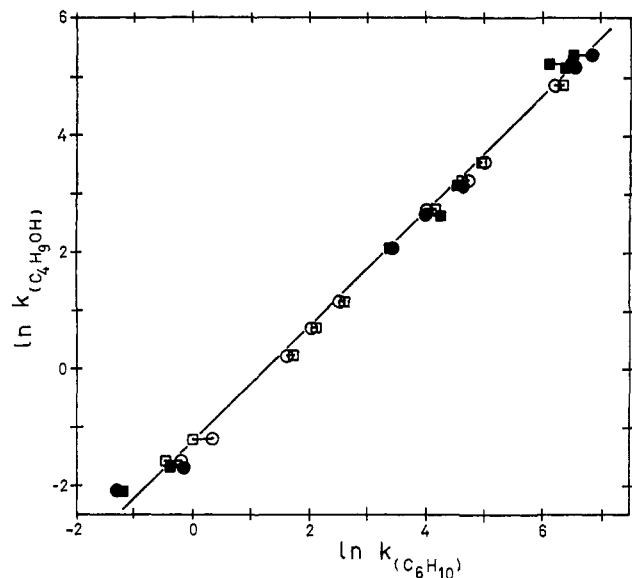


Figure 1. Comparative rate plot showing rate constants for the decomposition of *tert*-butyl alcohol as a function of rate constants for the decomposition of ethylene (circles) and 1,3-butadiene (squares) formation from the decyclization of cyclohexene: ○ and □ = 0.215% *tert*-butyl alcohol + 0.215% cyclohexene in argon; ● and ■ = 1.00% *tert*-butyl alcohol + 0.50% cyclohexene in argon.

the end of the shock tube directly into a Varian Aerograph Model 1440-20 chromatograph. The column was a 1/8 in. × 10 ft length of 20% polypropylene glycol saturated with AgNO<sub>3</sub> on 80-100 mesh Chromosorb W at 50°. Three or four analyses were usually run on each sample. Peak areas were determined by the "cut and weigh" method. Calibration samples were run before, after, and at intervals throughout each day's activity.

**Shock Conditions.** Experimental conditions are summarized in Table II. Gas temperatures behind reflected shocks were calculated by two independent methods: (a) from extents of ethylene and 1,3-butadiene formation from cyclohexene (if included), and (b) from measured incident shock velocities, using ideal one-dimensional theory. For the latter calculations, thermodynamic data for *tert*-butyl alcohol and cyclohexene were calculated from vibrational assignments given by Pritchard and Nelson<sup>17</sup> and Neto, *et al.*,<sup>18</sup> respectively. The cyclohexene decyclization is quite endothermic ( $\Delta H^{\circ}_{298} = +40.5$  kcal/mol) and the *tert*-butyl alcohol decomposition less so ( $\Delta H^{\circ}_{298} = +12.9$  kcal/mol). Shocks run at the high end of the temperature range (1175°K) in sets A and B resulted in approximately 20% conversion of *tert*-butyl alcohol and 50% conversion of cyclohexene. At these highest extents of conversion, enthalpies of reaction result in significant temperature changes in the reacting gas, up to about 15°K in set A and 30°K in set B. Thus effective gas temperatures, averaged over the reaction times, are a few degrees lower than values calculated from incident shock speeds. A computer program was written to calculate appropriate corrections for each reaction mixture over the temperature range covered; all temperature values deduced from shock speed measurements, given in Table II and elsewhere in this paper, have been corrected for enthalpies of reaction.

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

(18) N. Neto, C. DiLauro, E. Costellucci, and S. Califano, *Spektrochim. Acta, Part A*, **23**, 1763 (1967).

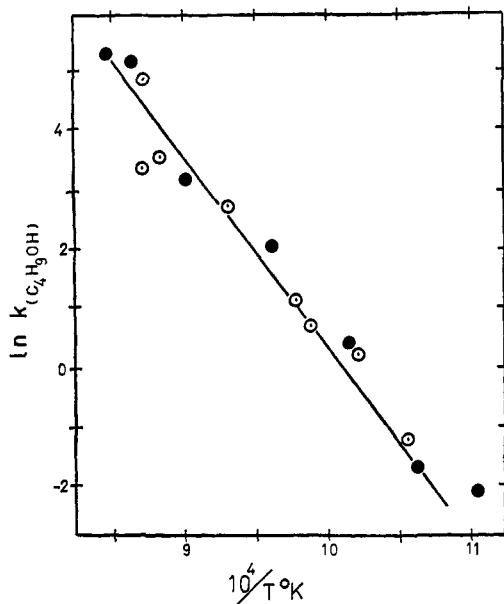
**Rate Calculations.** From each sample analysis, the rate constants for production of isobutene from *tert*-butyl alcohol, and ethylene and 1,3-butadiene from cyclohexene (if included) were calculated using the integrated rate expression for irreversible first-order reactions. At these low reaction pressures, the assumption of irreversibility introduces no significant error up to very large extents of reaction.

## Results

Quantification of products from shocks in which less than 0.01% of *tert*-butyl alcohol had been converted was difficult as the peak areas were subject to significant variations; consequently, a few experiments run below 920°K were dropped from consideration. Otherwise, the scatter between successive analyses of the same shocked gas sample was very small. Rate constants calculated from successive analyses were averaged. Production of allene and propylene as side products from *tert*-butyl alcohol was noted at temperatures above 1150°K. Allene amounted to about 10% of the isobutene at 1200°K (about 30% conversion of *tert*-butyl alcohol); and the allene/isobutene ratio increased at higher temperatures. Tsang<sup>3</sup> has postulated that these side products are formed from the main product, isobutene, but Mintz and Cvetanović<sup>19</sup> have since indicated that the side products may be due to the competing scission of a methyl group from *tert*-butyl alcohol:  $t\text{-C}_4\text{H}_9\text{OH} \rightarrow \text{CH}_3 + (\text{CH}_3)_2\text{COH}$ . They estimated that the percentage of *tert*-butyl alcohol decomposition attributable to this radical process is 0.3% at 700°K, 16% at 1000°K, 62% at 1300°K, and 95% at 2000°K. Because we cannot be certain of the origin of the side products, and because the predicted extent of bond scission would result in significant depletion of *tert*-butyl alcohol in experiments in which total extents of conversion exceeded 20%, runs at temperatures above 1175°K have also been dropped from consideration in the relative rate analysis. Only minor quantities of methane were observed as a side product of cyclohexene decomposition throughout the temperature range of this study. Amounts of ethylene and 1,3-butadiene produced over the range 920-1175°K were in close agreement; rate constants calculated from these two products differed by amounts which reflect less than a 10° difference, and in most cases less than a 5° difference, in gas temperature. No systematic deviation could be discerned.

Seventeen reliable experiments were considered from the two groups of relative rate experiments (sets A and B in Table II). Figure 1 shows the calculated rate constants for both reactions. All rate constants are in units of reciprocal seconds. As can be seen, there is no systematic difference between runs on the two sample mixtures. Linear least-squares treatment of the data gives a slope of 0.989 and an intercept of -1.241.

(19) K. J. Mintz and R. J. Cvetanović, *Can. J. Chem.*, **51**, 3386 (1973).



**Figure 2.** Rate constants for decomposition of *tert*-butyl alcohol vs.  $10^4/T^\circ\text{K}$ , with temperatures determined from incident shock speeds. Relative rate experiments (sets A and B):  $\circ$  = 0.215% *tert*-butyl alcohol + 0.215% cyclohexene in argon;  $\bullet$  = 1.00% *tert*-butyl alcohol + 0.50% cyclohexene in argon. Pressure range 670–940 Torr. The line is from the relative rate calculation.

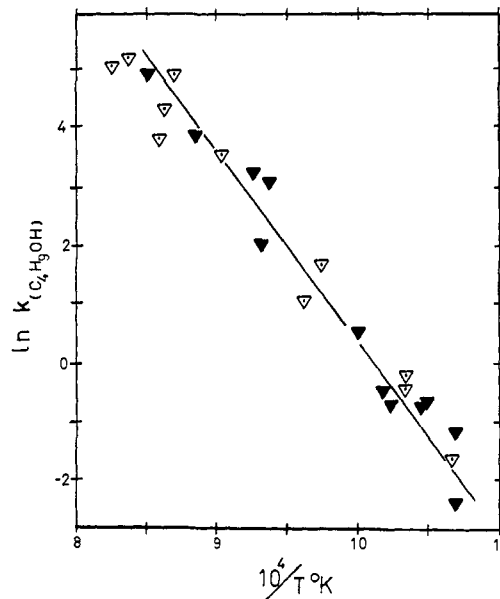
Using the rate parameters reported by Tsang<sup>13</sup> for cyclohexene pyrolysis,  $\log A = 15.3$  and  $E_a = 66.9$  kcal/mol, we obtained for the decomposition of *tert*-butyl alcohol to isobutene and water

$$\log k = (14.6 \pm 0.2) - [(66,200 \pm 1000)/4.58T^\circ\text{K}] \quad (925\text{--}1175^\circ\text{K}) \quad (1)$$

The uncertainties represent one standard deviation in the linear least-squares calculation, but obviously a larger uncertainty must be assumed, to reflect the additional uncertainty associated with the reported Arrhenius parameters of the standard reaction (see Discussion).

The rate constants for isobutene formation from the relative rate experiments are also shown on an Arrhenius plot in Figure 2. Here, the temperatures are those computed from measured incident shock velocities, corrected for enthalpy of reaction. The Arrhenius line determined from the relative rate calculation has been included, and this allows a comparison of temperature values calculated from shock speeds with values calculated from extents of cyclohexene decyclization. As can be seen, differences did not exceed  $\pm 30^\circ\text{K}$ . However, a least-squares line through the data points in Figure 2 gives an activation energy of  $58.1 \pm 3.7$  kcal/mol, compared with the  $66.2 \pm 1.0$  kcal/mol value obtained from the relative rate computation.

In Figure 3 we have plotted the rate constants for experiments from sets C and D, run on mixtures which contained only *tert*-butyl alcohol in argon. The experiments were run to be certain that there was no evidence of interaction between *tert*-butyl alcohol and cyclohexene in sets A and B and also to uncover any possible dependence of the reaction upon total pressure. A few high-temperature runs in which the total concentration of side products exceeded 5% of the isobutene concentration have again been discarded. These runs all showed shock speed temperatures above  $1200^\circ\text{K}$ . The



**Figure 3.** Rate constants for decomposition of *tert*-butyl alcohol vs.  $10^4/T^\circ\text{K}$ , with temperatures determined from incident shock speeds. Reference experiments (sets C and D):  $\nabla$  = 0.25% *tert*-butyl alcohol in argon, pressure range 1340–1560 Torr;  $\blacktriangledown$  = 1.03% *tert*-butyl alcohol in argon, pressure range 370–410 Torr. The line is from the relative rate calculation.

least-squares reduction of these data gives  $\log A = 12.5 \pm 0.5$  and  $E_a = 56.1 \pm 2.2$  kcal/mol. Again the relative rate results are also plotted in Figure 3 for comparison. As can be seen, there is no indication of dependence of reaction rate on total gas pressure. Also, a comparison of Figures 2 and 3 shows that there was apparently no significant interaction with the internal standard in sets A and B.

## Discussion

The results of earlier studies of the *tert*-butyl alcohol pyrolysis, summarized in Table I, are shown for comparison with the present relative rate results in an Arrhenius plot in Figure 4. The study by Dorko, *et al.*,<sup>4</sup> is not shown because the temperature range of their experiments was not reported; however, their data are essentially identical with Tsang's.<sup>3</sup> In comparing activation energies, the value reported by Schultz and Kistiakowsky<sup>1</sup> is in very good agreement with the present work, despite the large estimated uncertainty. Tsang's value<sup>3</sup> also agrees within the error limits. The study by Dorko, *et al.*,<sup>4</sup> was performed in a shock tube using measured shock speeds for temperature calculations. Considering the state of the art, the specified uncertainty listed in Table I is unrealistically small; the error limits reported by Tsang<sup>3</sup> seem more reasonable. The value reported by Barnard<sup>2</sup> is the only one that is clearly incompatible with the present relative rate result. There is no apparent explanation of this discrepancy. Barnard, discussing the earlier work of Schultz and Kistiakowsky,<sup>1</sup> suggested that those workers had obtained their high activation energy value as a result of the participation of free-radical side reactions, possibly caused by insufficient seasoning of the reaction flask. However, in the present study which gives a similar value, the homogeneous shock tube conditions, the lack of observed side products below  $1150^\circ\text{K}$ , and the presence of cyclohexene (a good inhibitor of free-radical

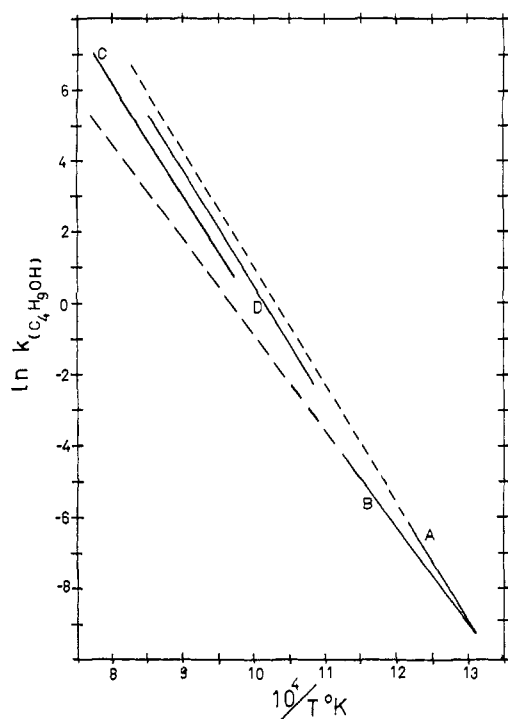


Figure 4. Comparison of rate constants for decomposition of *tert*-butyl alcohol as a function of  $10^4/T^\circ\text{K}$ : A from ref 1; B from ref 2; C from ref 3; D from this work, relative rate result.

processes) make it unlikely that free-radical processes contributed significantly to the measured rates. Also, extrapolation of Barnard's Arrhenius line to high temperatures predicts rate constants that are nearly an order of magnitude below those found in this study and also well below those determined by Tsang and by Dorko, *et al.* Tsang, in the analysis of the uncertainty associated with his results, estimated that his true temperatures were probably 10–25° below those calculated from incident shock speeds. Lowering his temperatures by 15° at 1050°K and 30° at 1200°K places his data in complete agreement with this relative rate study.

The possible influence of unimolecular falloff effects on the *tert*-butyl alcohol reaction in this study was investigated by application of RRK theory, as described in earlier work.<sup>10</sup> RRK theory was chosen over the more laborious RRKM theory as a result of the findings of Golden, *et al.*,<sup>20</sup> that the results are comparable. This generality has since been questioned by Skinner and Rabinovich,<sup>21</sup> who performed parallel RRK and RRKM calculations for *cis*-2-butene isomerization at at 742, 1300, and 2000°K. However, the discrepancies were large only at 742°K. Calculations performed for *tert*-butyl alcohol under experimental conditions of this study show that the reaction was essentially within the high-pressure region. Supporting evidence is offered by the experiments. Considering sets A–D, *tert*-butyl alcohol partial pressures ranged from 1.5 to 9 Torr, and argon diluent pressures ranged from 370 to 1560 Torr. No detectable falloff was observed at the lower pressures. Note that the parameters reported here (eq 1) were deduced from sets A and B only, which were run with argon pressures of 670 to 940 Torr, and which

(20) D. M. Golden, R. K. Solly, and S. W. Benson, *J. Phys. Chem.*, **75**, 1333 (1971).

(21) G. B. Skinner and B. S. Rabinovitch, *J. Phys. Chem.*, **76**, 2418 (1972).

contained 1.5 to 4.5 Torr of cyclohexene in addition to the *tert*-butyl alcohol. Also, these total pressures are well above the pressure, 3 Torr, at which Schultz and Kistiakowsky<sup>1</sup> detected the onset of falloff at 789°K.

The  $\pm 30^\circ$  consistency between reflected shock temperature values calculated from incident shock velocities and from cyclohexene decomposition in this study is gratifying considering the  $\pm 25^\circ$  to  $\pm 50^\circ$  scatter that seems to be inherent in shock tube data when temperatures are determined from shock speeds. However, the considerable difference between the activation energy value based upon shock speed temperatures and the value derived from the relative rate analysis demands a careful assessment of the reliability of the relative rate result in eq 1. The absolute rate value from sets A and B differs from the relative rate value by two standard deviations (95% confidence level). We feel that the extreme linearity and lack of scatter of Figure 1 support the validity of this relative rate study, but if there are errors in the kinetic parameters assumed for the standard reaction, these errors will of course be passed on to the derived parameters for the reaction under study. Tsang's reported parameters for cyclohexene, and the derived *tert*-butyl alcohol parameters in eq 1, are supported by the following considerations.

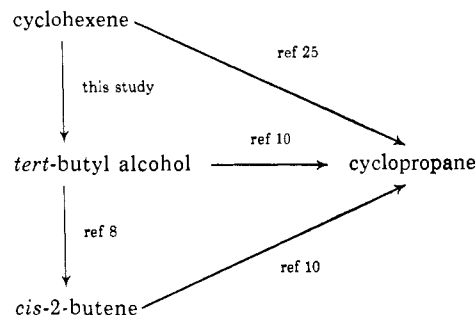
(1) Tsang performed two independent relative rate studies to determine the Arrhenius parameters for cyclohexene decyclization.<sup>12,13</sup> In the first,<sup>12</sup> the unimolecular dehydrogenation of isopropyl chloride was used as a standard. The rate parameters for this reaction had been determined in an earlier relative rate study against isopropyl bromide decomposition<sup>22</sup> and were found to be in excellent agreement with the most reliable literature data. In the second cyclohexene study,<sup>13</sup> Tsang used as a standard the unimolecular decyclization of ethylcyclobutane; the parameters for this reaction were obtained by Wellman and Walters.<sup>23</sup> The two cyclohexene studies gave essentially identical Arrhenius parameters, and these agree very well with an extrapolation of the lower temperature results of Uchiyama, Tomioka, and Amano.<sup>14</sup> Tsang has estimated the total uncertainties in the parameters for cyclohexene as  $A \pm 0.2$  and  $E_a \pm 800$  cal/mol. It should, of course, be noted that these parameters depend ultimately upon the extrapolations of lower temperature results for isopropyl bromide, isopropyl chloride, ethylcyclobutane, and cyclohexene to the considerably higher temperatures employed in shock tube work. However, it seems unlikely that the good agreement between Tsang's shock tube data and the extrapolation from lower temperature work for all these reactions could be coincidental. Further support is offered by the lack of systematic differences between the absolute and relative rate data in Figures 2 and 3; large errors in the cyclohexene parameters due to improper extrapolation of low-temperature results would have resulted in a displacement of our relative rate data from the absolute data.

(2) A relative rate study of the structural isomerization of cyclopropane to propylene, using *tert*-butyl alcohol as the internal standard, has been performed in this laboratory.<sup>10</sup> The Arrhenius parameters deduced for cyclopropane, based on the *tert*-butyl alcohol parameters given in eq 1, are in perfect agreement with Benson

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and O'Neal's<sup>24</sup> preferred values based on low-temperature data for this reaction. Furthermore, Jeffers<sup>10</sup> and Jeffers, *et al.*,<sup>25</sup> obtained the same values for cyclopropane isomerization in relative rate experiments using isomerization of *cis*-2-butene and decyclization of cyclohexene as the standard reactions. The parameters for *cis*-2-butene were based on an earlier *cis*-2-butene *vs.* *tert*-butyl alcohol relative rate study and the *tert*-butyl alcohol parameters in eq 1. These studies complete two circles, with excellent consistency.



The tail of each arrow represents the reference compound and the head of the arrow the unknown.

(3) At this time we have completed two other relative rate studies: cyclopentene dehydrogenation (*vs.* *tert*-butyl alcohol)<sup>11</sup> and *tert*-butyl methyl ether decomposition (*vs.* cyclohexene).<sup>26</sup> In both cases, Arrhenius parameters agree well with extrapolation of lower temperature data when the *tert*-butyl alcohol parameters in eq 1 and Tsang's cyclohexene parameters are assumed.

(4) Two other absolute rate studies<sup>5,6</sup> run in shock tubes believed to be in good working order gave rate constants for *tert*-butyl alcohol decomposition that are more consistent with eq 1 than with the shock tube results of Tsang<sup>3</sup> or Dorko.<sup>4</sup>

There are, however, two factors which suggest that the 66.2 kcal/mol activation energy value in eq 1 may be slightly too high. First, extrapolation of the relative rate results to lower temperature (Figure 4) does not give perfect agreement with the low-temperature work. A line which connects the center of the relative rate line (1050°K) with the point of intersection of the two low-temperature studies (760°K) gives  $E_a = 63$  kcal/mol. Second, the results of Jeffers and Shaub's<sup>8</sup> study of *cis*-2-butene isomerization *vs.* *tert*-butyl alcohol decomposition give for the former reaction  $\log A = 14.6$  and  $E_a = 66.2$  kcal/mol, based on the *tert*-butyl alcohol parameters in eq 1. These parameters for *cis*-2-butene are in good agreement with the values ( $\log A = 14.54$  and  $E_a = 65.0$  kcal) obtained by Lifshitz, *et al.*,<sup>15</sup> by connecting shock tube data with low-temperature rate constants reported by Rabinovitch and Michel<sup>27</sup> and Cundall and Palmer,<sup>28</sup> but they are considerably higher than the values determined from the low-temperature data alone ( $\log A = 13.78$ ,  $E_a = 62.8$  kcal,<sup>27</sup> and  $\log A = 14.00$ ,  $E_a = 62.4$  kcal<sup>28</sup>). They are also higher than those predicted by Benson:<sup>29,30</sup>  $\log A = 13.3$  and  $E_a =$

61.7 kcal. With regard to the latter comparison, it should be noted there is a still larger discrepancy, in the same direction, between predicted<sup>30</sup> and experimental<sup>31</sup> parameters for *cis*-stilbene isomerization (predicted/measured:  $\log A = 10.9/12.8$ ;  $E_a = 33.5/42.8$  kcal) although this may simply indicate a need for better experimental data.

It should be mentioned that Jeffers and Shaub<sup>8</sup> and Jeffers<sup>9</sup> have also reported high-pressure rate constants for six other unimolecular *cis*-*trans* isomerizations which they determined *via* the relative rate shock tube method using *cis*-2-butene as the standard. If the reported Arrhenius parameters for these reactions are adjusted upward with those for *cis*-2-butene isomerization, agreement with extrapolation of lower temperature work is improved for one (*cis*-1,2-dichloroethylene isomerization) and reduced for another (*trans*-perfluoro-2-butene isomerization). However, the possible accumulation of small systematic errors in the series of determinations isopropyl chloride and ethylcyclobutane  $\rightarrow$  cyclohexene  $\rightarrow$  *tert*-butyl alcohol  $\rightarrow$  *cis*-2-butene  $\rightarrow$  x makes such comparisons of uncertain validity.

Assuming that the comparative rate study reported here is sound, we can only speculate on the possible sources of error in the absolute rate measurements. Our shock tube's experimental section has a length that is 36.6 times the tube diameter, slightly shorter than the 40–60  $\times$  diameter range considered desirable for a single pulse tube. It is possible that the shock front was not well formed in the higher temperature experiments. However, there was no evidence of this from the pressure histories, nor was there any visible evidence of pressure changes behind the reflected shocks or of early onset of cooling due to improper tuning of the tube. The presence of boundary layer gas in the analyzed samples always introduces some error, but the large tube diameter, short reaction times, and low extents of conversion of *tert*-butyl alcohol (<20%) should have made this error negligible.

The most likely source of error, we feel, is partial mixing of the cooled gas by subsequent waves not completely attenuated by the damping tank. Extended time pressure records do show one or more weak compression/expansion sequences after the initial one; the number of detectable aftershocks varies from one at 900°K to three at 1200°K. Although these are far too weak to reheat the gas to reaction temperatures, they could induce a slight oscillating gas flow which might cause some mixing of the gas. Since the sampling port is near the downstream end of the tube, the effect of this mixing would be to introduce into the analyzed samples some gas which had not been heated for the full measured reaction time. This would lower the calculated values of the rate constant. This error would be expected to increase with temperature, for the following reason. The initial gas pressures in the shock tube experimental section were lowest for the high end of the temperature range, while the driver gas pressure was essentially constant for all runs in each group. Therefore, the products of high-temperature runs occupied

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smaller volumes near the downstream end of the experimental section than did the products of low-temperature runs. Since quantities of product with significantly different reaction times were closest together following high-temperature runs, the lowering of calculated rate constants due to mixing would be largest for these runs, even if the extent of mixing were the same for all runs. From the pressure histories it seems likely that the extent of mixing, if any, would have increased with increasing reflected shock temperature: this would increase the error at the high end of the temperature range. We cannot assess the magnitude of mixing except to note that it was not extensive enough to introduce detectable amounts of driver gas into the product samples. However, as mixing should have no significant effect on the comparative rate analysis, this could explain the small divergence between comparative and absolute rate results in the 1100–1175° region and the resulting difference in activation energy values.

From our data and the arguments discussed above, we feel that the activation energy for *tert*-butyl alcohol decomposition to isobutene and water lies somewhere between 63.0 and 66.2 kcal/mol. Because the 66.2-kcal/mol value results in the best internal consistency among the many comparative rate experiments discussed in this report and leads to deduced parameters for a number of reactions that agree well with extrapolations of low-temperature work,<sup>10,11,26</sup> we favor the higher end of the acceptable range.

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## Boron-11 Nuclear Magnetic Resonance Chemical Shift Assignments for Monohalogenated Decaborane(14) Isomers

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**Abstract:** Boron-11 nmr chemical shifts have been assigned for all possible isomers of monochloro-, monobromo-, and moniododecaborane(14) using the <sup>11</sup>B–<sup>11</sup>B double resonance technique. The properties of 5-chlorodecaborane(14) and 6-iododecaborane(14) were reported for the first time. Chemical shifts are found to depend on the halogen and the site of substitution in a regular manner. All shift trends are dominated by the influence of the 2p orbital size on the paramagnetic shielding term ( $\sigma_p$ ). It was suggested that a small  $\sigma_p$  accounts for the shielding of B<sub>2</sub> and B<sub>3</sub> relative to the rest of the cage.

Theories of the origin of the nmr chemical shift have been proposed by Saika and Slichter,<sup>2a</sup> Karplus and Das,<sup>2b</sup> and Pople.<sup>3</sup> In all of those treatments, the shielding at a particular atom was found to be separable into a diamagnetic atomic term, a paramagnetic atomic term, and a term due to neighboring atoms. Applications of these theories to <sup>13</sup>C chemical shifts by Karplus and Pople,<sup>4</sup> Pople,<sup>5</sup> and Cheney and Grant,<sup>6</sup> to <sup>11</sup>B chemical shifts by Boer, *et al.*,<sup>7</sup> to <sup>14</sup>N chemical shifts by Kent and Wagner,<sup>8</sup> to <sup>17</sup>O chemical shifts by Moniz and Poranski,<sup>9</sup> and to <sup>19</sup>F chemical shifts by Saika and Slichter<sup>2a</sup> and Karplus and Das<sup>2b</sup> has resulted in confirmation of the theory and explanation of many em-

pirical correlations. The theory has been extended to include the effects of bonding through d orbitals by Jameson and Gutowsky,<sup>10</sup> who also discussed periodicities in the ranges of chemical shifts in terms of an explicit dependence of the paramagnetic term on the nuclear charge. A recent study of decaborane(14) by Laws, *et al.*,<sup>11</sup> gives a detailed picture of the electronic structure of the molecule but unfortunately does not give much attention to the problem of <sup>11</sup>B chemical shifts.

### I. Discussion

We have assigned all <sup>11</sup>B nmr chemical shifts for all of the monochloro-, monobromo-, and moniododecaboranes, using a double resonance technique,<sup>12</sup> and have compared the shifts with those of the parent compound. In order to explain the trends we see, one must assume that the contribution of the paramagnetic part of the

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